

# **APPLIED** *Spectroscopy*



1961

Vol. 15 No. 2

REPRINT

PUBLISHED BY THE SOCIETY FOR APPLIED SPECTROSCOPY





APPLIED SPECTROSCOPY is a bimonthly publication of the Society for Applied Spectroscopy. Formerly called the BULLETIN OF THE SOCIETY FOR APPLIED SPECTROSCOPY, the volume numbers are a continuation of those of the BULLETIN.

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April Issue—Published Bimonthly—  
Vol. 15, No. 2, 1961  
Second Class Postage  
Paid at Plainfield, N. J.  
Known office of publication: P.O. Box 1228,  
417 Cleveland Avenue, Plainfield, New Jersey  
POSTMASTER: Send form 3579 to the publication office.  
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APPLIED  
Spectroscopy

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## APPLIED SPECTROSCOPY

Published by the Society for Applied Spectroscopy

Volume 15

No. 2, 1961

Infrared Spectral-Structural Correlations  
of Some Substituted Pyridines†

Edith M. Godar\* and Raymond P. Mariella\*\*

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## Abstract

Three series of substituted pyridines have been prepared having substituents in various positions on the ring. Although there were variations in the chemical nature and in the position of these substituents, it was found that certain fundamental absorption bands are typical of all the pyridines studied. The separation of the two bands in the 1600-1500  $\text{cm}^{-1}$  region does not appear to be helpful in determining the position of substituents, but absorption in the 950-750  $\text{cm}^{-1}$  region does give a clue as to the number of adjacent hydrogens on the pyridine ring. There appears to be a band very characteristic of the cyclohexeno ring, thus confirming previous work. In addition, a band was found which is due to the cyclohexeno ring, as modified by the attached pyridine ring. There seems to be absorption characteristic of the cyclohepteno ring. Correlation is made of the several substituent groups when attached to the pyridine ring, as compared to the same groups attached to the benzene ring.

The characteristic features of the infrared spectra of benzene and related aromatic compounds are reasonably well known because of the large number of such compounds that have been studied and reported in the literature. Unfortunately, the infrared spectra of the heterocyclic aromatic nitrogen compounds, such as pyridines and quinolines, are not as well characterized as the mono-substituted pyridines.

The infrared spectra of a number of alkyl pyridines have been studied and reported (1-6) and a recent paper has been concerned with the spectra-structure correlations of quinolines (7). The present work is concerned with the correlation of the infrared spectra of variously substituted pyridines with the degree of substitution and the position of the substituents.

Previous work (8) along this same line has shown that in pyridines substituted in the 2,3-positions by methyl groups or by carboxylic rings of varying size, the nature of the substituents caused significant shifts in the ring vibration and hydrogen deformation frequencies. Smaller

absorption band shifts were also noted in the other regions of the spectrum.

## Experimental

The majority of the compounds whose spectra were recorded were solid materials. The low-melting compounds were run as melts, the higher melting compounds as Nujol mulls and/or in potassium bromide pellets. No significant shifts in absorption band maxima were noticed in any of the compounds on changing from a Nujol mull to a potassium bromide pellet. All infrared spectra were recorded using a Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with a sodium chloride prism.

## Results and Discussion

In the high frequency region of the infrared spectrum, all the compounds studied show a high degree of similarity. As may be seen from Table I (formulae in Figure 1), all the compounds have absorption bands near 1600, 1550, 1500, and 1200  $\text{cm}^{-1}$ . Another band which is fairly con-

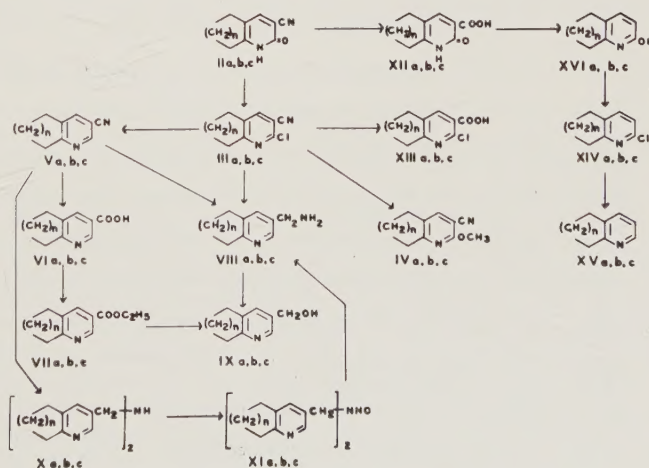
FOR "a" COMPOUNDS  $n = 1$ . FOR "b" COMPOUNDS  $n = 2$ . FOR "c" COMPOUNDS  $n = 3$ 

FIG. 1. STRUCTURAL FORMULAE OF COMPOUNDS INCLUDED IN TABLE I

(Continued on page 31)

†Abstracted from the Dissertation of Edith M. Godar, submitted in February 1959 in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented at the Tenth Annual Symposium, Chicago Section, Society for Applied Spectroscopy, June 4, 1959.

\*Dreyfus Foundation Fellow, 1956-1958

\*\*To whom all inquiries should be sent. The details concerning the preparation of the compounds in this paper will be published elsewhere.



TABLE I. BANDS TYPICAL OF PYRIDINES<sup>a</sup>

Code	Compound	Band No.							
		1	2	3	4	5	6	7	8
XIVa	6,7-Dihydro-2-chloro-1,5-pyridine	3090	1594	1575	1468	1180	1088	842	720
XIVb	5,6,7,8-Tetrahydro-2-chloroquinoline	3070	1590	1572	1467	1195	1102	858	716
XIVc	6,7,8,9-Tetrahydro-2-chloro-5H-cyclohepta[b]pyridine	3080	1570	1558	1468	1170	1078	848	710
XVIa	6,7-Dihydro-1,5-pyridine-2-ol	3090	1610	1570	1482	1173		842	725
			1630						
XVIb	5,6,7,8-Tetrahydroquinoline-2-ol	3050	1640	1562	1460	1198		854	722
XVIc	6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-2-ol	3020	1613	1560	1468	1190		866	731
IIIa	6,7-Dihydro-2-chloro-3-cyano-1,5-pyridine		1594	1540		1157	1020	938	699
IIIb	5,6,7,8-Tetrahydro-2-chloro-3-cyanoquinoline		1593	1543		1171	1040	949	694
			1580						
IIIc	6,7,8,9-Tetrahydro-2-chloro-3-cyano-5H-cyclohepta[b]pyridine		1595	1548		1160	1036	935	699
IVa	6,7-Dihydro-2-methoxy-3-cyano-1,5-pyridine		1607	1570		1217	1007	933	762
IVb	5,6,7,8-Tetrahydro-2-methoxy-3-cyanoquinoline		1605	1570		1210	1007	934	757
IVc	6,7,8,9-Tetrahydro-2-methoxy-3-cyano-5H-cyclohepta[b]pyridine		1602	1570		1195	1002	930	776
XIIIa	6,7-Dihydro-2-chloro-1,5-pyridine-3-carboxylic acid	3030	1608	1571	1468	1160	1130	923	762
XIIIb	5,6,7,8-Tetrahydro-2-chloroquinoline-3-carboxylic acid	3050	1602	1563	1470	1178	1148	939	742
XIIIc	6,7,8,9-Tetrahydro-2-chloro-5H-cyclohepta[b]-pyridine-3-carboxylic acid		1597	1560	1460	1170	1150	932	742
IIa	6,7-Dihydro-3-cyano-1,5-pyrid-2-one	3040	1616	1589	1465	1150		958	773
IIb	5,6,7,8-Tetrahydro-3-cyano-2-quinolone	3050	1627	1580	1465	1150		964	770
IIc	6,7,8,9-Tetrahydro-3-cyano-5H-cyclohepta[b]-2-pyridone	3050	1600	1570	1460	1156		965	774
XIIa	6,7-Dihydro-1,5-pyrid-2-one-3-carboxylic acid	3040	1620	1564	1486	1181		940	725
XIIb	5,6,7,8-Tetrahydro-2-quinolone-3-carboxylic acid	3060	1620	1562	1480	1198		933	724
XIIc	6,7,8,9-Tetrahydro-5H-cyclohepta[b]-2-pyridone-3-carboxylic acid	3050	1615	1564	1472	1178		960	725
VIa	6,7-Dihydro-1,5-pyridine-3-carboxylic acid	3070	1610	1560	1472	1195	1050	935	774
VIb	5,6,7,8-Tetrahydroquinoline-3-carboxylic acid	3060	1610	1588	1460	1174	1065	945	764
VIc	6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-3-carboxylic acid	3050	1613	1590	1472	1200	1025	930	755
VIa	6,7-Dihydro-1,5-pyridine-3-carboxylic acid hydrochloride		1640	1548		1180	1045	910	760
VIb	5,6,7,8-Tetrahydroquinoline-3-carboxylic acid hydrochloride		1628	1562		1160	1018	917	760
			1640						
VIc	6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-3-carboxylic acid hydrochloride <sup>a</sup>		1624	1560		1159	1020	915	763
			1640						
VIIIa	6,7-Dihydro-3-aminomethyl-1,5-pyridine		1612	1580	1478	1220	1040	897	720
VIIIb	5,6,7,8-Tetrahydro-3-aminomethylquinoline	3020	1611	1576	1475	1202	1053	922	712
VIIIc	6,7,8,9-Tetrahydro-3-aminomethyl-5H-cyclohepta[b]pyridine	3040	1610	1575	1473	1192	1072	910	709
VIIa	6,7-Dihydro-3-aminomethyl-1,5-pyridine dihydrochloride	3030	1635	1553	1470	1173	1050	896	737
			1650	1525					
VIIIb	5,6,7,8-Tetrahydro-3-aminomethylquinoline dihydrochloride	3080	1620	1570	1470	1160	1055	928	720
			1640						
VIIIc	6,7,8,9-Tetrahydro-3-aminomethyl-5H-cyclohepta[b]pyridine dihydrochloride	3030	1627	1570	1462	1150	1076	928	715
			1640	1502					
VIIa	6,7-Dihydro-3-carboethoxy-1,5-pyridine	3090	1610	1575	1485	1185	1026	950	778
VIIb	5,6,7,8-Tetrahydro-3-carboethoxyquinoline	3000	1613	1580	1470	1175	1027	945	770
VIIc	6,7,8,9-Tetrahydro-3-carboethoxy-5H-cyclohepta[b]pyridine	3000	1613	1577	1472	1202	1032	932	777
Va	6,7-Dihydro-3-cyano-1,5-pyridine		1600	1558		1240	1032	913	712
Vb	5,6,7,8-Tetrahydro-3-cyanoquinoline		1604	1560		1202	1006	932	706
Vc	6,7,8,9-Tetrahydro-3-cyano-5H-cyclohepta[b]pyridine		1600	1562		1198	1074	919	708
IXa	6,7-Dihydro-3-hydroxymethyl-1,5-pyridine		1620	1590		1220	1036	890	720
IXb	5,6,7,8-Tetrahydro-3-hydroxymethylquinoline		1610	1580	1480	1202	1006	916	712
IXc	6,7,8,9-Tetrahydro-3-hydroxymethyl-5H-cyclohepta[b]pyridine		1612	1582	1478	1227	1025	903	715
IXa	6,7-Dihydro-3-hydroxymethyl-1,5-pyridine hydrochloride		1635	1560		1220	1048	891	742
			1648						
IXb	5,6,7,8-Tetrahydro-3-hydroxymethylquinoline hydrochloride		1630	1563		1230	1038	899	748
			1640						
IXc	6,7,8,9-Tetrahydro-3-hydroxymethyl-5H-cyclohepta[b]pyridine hydrochloride		1628	1570		1210	1018	893	733
			1640						
Xa	Di-([6,7-dihydro-1,5-pyridine- $\beta$ -yl)methyl) amine	3040	1613	1580	1468	1204	1112	910	721
Xb	Di-([5,6,7,8-tetrahydroquinol- $\beta$ -yl)methyl) amine	3030	1610	1580	1490	1210	1115	917	713
								922	
Xc	Di-([6,7,8,9-tetrahydro-5H-cyclohepta[b]pyrid- $\beta$ -yl)methyl) amine	3020	1616	1580	1478	1206	1097	905	713
								916	
Xa	Di-([6,7-dihydro-1,5-pyridine- $\beta$ -yl)methyl) amine monohydrochloride		1619	1582	1470	1218	1038	902	722
								910	
Xb	Di-([5,6,7,8-tetrahydroquinol- $\beta$ -yl)methyl) amine monohydrochloride		1614	1583	1468	1210	1020	922	712
								924	
Xc	Di-([6,7,8,9-tetrahydro-5H-cyclohepta[b]pyrid- $\beta$ -yl)methyl) amine monohydrochloride		1612	1575	1474	1242	1058	903	710
								913	
XIa	Di-([6,7-dihydro-1,5-pyrid- $\beta$ -yl)methyl) N-nitrosamine	3060	1610	1581	1478	1248	1130	920	735
								933	
XIb	Di-([5,6,7,8-tetrahydroquinol- $\beta$ -yl)methyl) N-nitrosamine	3040	1610	1573	1474	1245	1125	922	724
								933	
XIc	Di-([6,7,8,9-tetrahydro-5H-cyclohepta[b]pyrid- $\beta$ -yl)methyl) N-nitrosamine	3010	1610	1578	1478	1265	1129	922	722
								935	
XVa	6,7-Dihydro-1,5-pyridine	3000	1587	1570	1463	1214	1088	786	722
XVb	5,6,7,8-Tetrahydroquinoline	3030	1585	1570	1450	1184	1112	782	728
XVc	6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine	3085	1588	1576	1457	1193	1085	793	767
								803	
XVb	5,6,7,8-Tetrahydroquinoline hydrochloride	3080	1620	1553	1460	1170	1080	802	723
								795	
								790	

<sup>a</sup> Absorption maxima in cm<sup>-1</sup> and formulae given in Figure 1.



(Continued from page 29)

stant occurs in the 1110-1000  $\text{cm}^{-1}$  region. The two remaining bands which may be taken as typical of the pyridine ring system occur at lower wave numbers and show a much wider variation in position.

### C=C, C=N Stretching Vibrations

Shindo and Ikekawa (3) made an attempt to explain the positions of the two bands in the 1600-1500  $\text{cm}^{-1}$  region by considering changes in the electronic symmetry of the pyridine ring when substituted by methyl groups in various positions. They concluded that the appearance of the spectra in this region could not be explained as being due to such an effect since several anomalies were noted. Although they found no constant correlations between the frequency of absorption and the structure of the molecules, they state that the relative intensity of the two bands appeared to be determined by the relative position of the methyl groups to the nitrogen.

The relative intensity of the two bands also has been correlated to the electronegativity of the substituent group by a number of authors. Shindo (9) noted that in those 13-monosubstituted pyridines with electron donor substituents, the lower frequency band was the stronger of the pair, and with electron acceptor substituents, the reverse was true. Katritzsky, Hands, and Jones (5) remark that the higher frequency band of monosubstituted pyridines is of much higher intensity with both electron donor substituents and with strong electron acceptor substituents than with substituents of a more neutral character.

In our work the correlation of the relative intensity of these two bands with the electronegativity of the substituent also holds fairly well for the trisubstituted compounds. There is a noticeable but variable effect due to the size of the attached ring on the pyridine nucleus. In general, it would appear that the cyclopenteno ring is a weaker electron donor than the cyclohexeno or cyclohepteno rings.

No absolute intensity values were obtained, as the samples were not of uniform thickness. In general, the results are the expected ones in that the  $-\text{COOH}$ ,  $-\text{COOC}_2\text{H}_5$ , and the  $-\text{CN}$  groups are electron acceptors, and the compounds containing the other substituents are either of a fairly neutral character or act as electron donors.

### C—H In-Plane Bending Vibrations

Pyridine and alkylpyridines have been found to have fairly strong bands in these two regions of the infrared spectrum. The position of the spectra of the pyridine compounds included here show two fairly strong bands, one near 1200  $\text{cm}^{-1}$  and the other between 1100 and 1000  $\text{cm}^{-1}$ . The ranges found for the positions of these bands were extremely broad, so that it is doubtful if they would be of any aid in the assignment of a substitution pattern of an unknown compound.

All the compounds studied had absorption bands in the 1200  $\text{cm}^{-1}$  region, but there were a number of exceptions noted in the 1100-1000  $\text{cm}^{-1}$  region. None of the compounds containing the pyridone structure had strong absorption bands in the 1100-1000  $\text{cm}^{-1}$  region. The pyridones are not true aromatic compounds in that they have only two "double bonds" in the ring. Some of these pyridones give the usual ferric chloride test for phenols in solution, but the infrared spectra of all the 2-hydroxy compounds show them to contain a keto group in the solid state. Therefore they exist in the amide configuration in the crystalline state. These compounds also show the typical amide bands in the 1500  $\text{cm}^{-1}$  region, in con-

trast to the other compounds studied, which have no strong bands in this portion of the spectrum.

### C—H Out-of-Plane Bending Vibrations

The wave numbers of the out-of-plane hydrogen deformation vibrations occurring in this region of the spectrum may be correlated with the number and position of the substituents on the aromatic nucleus in both benzene and pyridine derivatives. The positions of these absorption bands as appearing in benzene compounds have been fairly well established, but there appears to be a wider variation with the aromatic heterocyclic compounds. Some recent data with regard to pyridine compounds has been obtained from the studies with alkyl substituted compounds (10).

Bellamy (11) has published some data relating the position of the deformation vibration of substituted benzenes with Hammett's substitution constants. The positions of these bands would be expected to be affected by the polarity and position of the substituent in pyridines also, although the relationship would be more complex than found with the benzenes due to the effect of the ring nitrogen.

The position of this band in the spectra of the 2,3,5,6-tetrasubstituted compounds was found in the range of 965-923  $\text{cm}^{-1}$  (one hydrogen). The range quoted by Bellamy (12) for one hydrogen on the pyridine nucleus is 900-850  $\text{cm}^{-1}$  for alkyl pyridines. Shindo and Ikekawa (3) report a range of 905-839  $\text{cm}^{-1}$  for eight polysubstituted methyl pyridines with one free hydrogen. They found that replacing the methyl groups with ethyl groups displaced the wave numbers to a higher value. The amount of shift was variable and depended on the position of the substituents on the ring.

The compounds substituted in the 2,3,5-positions included in Table I show absorption bands appearing in the range 950-890  $\text{cm}^{-1}$ . The secondary amines and nitroso compounds had two bands in this region of about equal intensity separated by 5-13  $\text{cm}^{-1}$ . The compounds comprising any one series usually absorbed over a fairly narrow range.

For the three series of 2,3,6-trisubstituted compounds prepared here, the position of the absorption band was found to vary from 866-842  $\text{cm}^{-1}$ . These compounds contain two adjacent hydrogen atoms on the pyridine ring. For methyl pyridines with two adjacent hydrogens, the range 821-793  $\text{cm}^{-1}$  is given by Shindo and Ikekawa (3). Bellamy (12) gives a figure of about 800  $\text{cm}^{-1}$ .

### Bands Typical of the Cyclohexeno Ring

In addition to the series of absorption bands which have been listed above as being typical of pyridine compounds, all the substituted pyridines with a cyclohexeno ring in the 2,3-position of the pyridine nucleus contain additional bands which are common to this type of compound. Bellamy (12) cites a reference by Marrison (13) who has noted that all published spectra of cyclohexane derivatives show bands in the ranges 1005-952  $\text{cm}^{-1}$  and 1055-1000  $\text{cm}^{-1}$ . Two exceptions were noted in a series of fifty compounds examined, and each of these exceptions had one of the bands. About half the compounds containing a six-membered ring contain bands in these two regions of the spectrum. The other half of the compounds have one or the other of these bands. In addition to these two bands which have previously been noted in the literature, another absorption band appeared in the spectra of all the prepared compounds. This band appeared in the narrow range of 832-818  $\text{cm}^{-1}$  and is in-



TABLE II. BANDS TYPICAL OF CYCLOHEXENO RING

Compound	Frequency, $\text{cm}^{-1}$		
5,6,7,8-Tetrahydro-2-chloroquinoline	832	988	
5,6,7,8-Tetrahydroquinoline-2-ol	820	990	
5,6,7,8-Tetrahydro-2-chloroquinoline-3-carboxylic acid	822	955	1032
5,6,7,8-Tetrahydro-2-methoxy-3-cyanoquinoline	828	955	1007, 1013
5,6,7,8-Tetrahydro-2-quinoline-3-carboxylic acid	818	965	
5,6,7,8-Tetrahydro-2-chloro-3-cyanoquinoline	828	950	1040
5,6,7,8-Tetrahydro-3-cyano-2-quinoline	820	965	
5,6,7,8-Tetrahydro-2-cyanoquinoline	823		1007
5,6,7,8-Tetrahydro-3-aminomethylquinoline dihydrochloride	828	982	1010
5,6,7,8-Tetrahydro-3-aminomethylquinoline	825		1007
5,6,7,8-Tetrahydro-3-hydroxymethylquinoline hydrochloride	825	997	1034
5,6,7,8-Tetrahydro-3-hydroxymethylquinoline	825	1005	1037
5,6,7,8-Tetrahydroquinoline-3-carboxylic acid	827		1010
5,6,7,8-Tetrahydroquinoline-3-carboxylic acid hydrochloride	822	970	1018
5,6,7,8-Tetrahydro-3-carboethoxyquinoline	828	1005	1027
Di-([5,6,7,8-tetrahydroquinolin- $\beta$ -yl)methyl)amine	825		1007
Di-([5,6,7,8-tetrahydroquinolin- $\beta$ -yl)methyl)amine hydrochloride	828	983	1020
Di-([5,6,7,8-tetrahydroquinolin- $\beta$ -yl)methyl)N-nitrosamine	825	965	1008
5,6,7,8-Tetrahydroquinoline	828	988	1050
5,6,7,8-Tetrahydroquinoline hydrochloride	818	993	1029

cluded in Table II. This third band is probably due to the cyclohexeno ring as modified by the attached pyridine ring. Neither cyclohexane nor cyclohexanone have any absorption bands in this region.

#### Bands Due to the Cyclohepteno Ring

The spectra of all the cyclohepteno pyridine compounds have two absorption bands in the low wave number region. These bands do not appear in the spectra of the other two series of compounds prepared and therefore must be peculiar to the cyclohepteno pyridine system. They appear in the  $840\text{--}827\text{ cm}^{-1}$  and  $777\text{--}718\text{ cm}^{-1}$  regions. The former region is of slightly higher wave number than the corresponding bands shown in the spectra of cyclohexeno pyridine compounds. In common with the cyclohexeno compounds, the pyridones absorb at the lowest wave numbers, i.e.  $830\text{--}827\text{ cm}^{-1}$ . The four compounds whose spectra were also recorded as the hydrochlorides absorb at the same position,  $836\text{--}835\text{ cm}^{-1}$ , although the free bases of the compounds have absorption bands appearing from  $838\text{--}832\text{ cm}^{-1}$ . These bands are all of medium intensity.

The absorption bands occurring in the  $777\text{--}718\text{ cm}^{-1}$  region are in general more intense than the higher wave number bands noted above. Here the bands of the pyridone compounds appear at lower wave numbers than do the other compounds. These pyridones absorb at  $732\text{--}718\text{ cm}^{-1}$ , the hydrochlorides of the four compounds recorded appear at  $762\text{--}754\text{ cm}^{-1}$ , with all but one of the other

compounds having bands appearing from  $777\text{--}762\text{ cm}^{-1}$ . The wave numbers of these two bands are given in Table III.

#### The Nitrile Group

The absorption frequency of the band due to the nitrile group shifts to lower values with increasing conjugation (12). In the four series of compounds prepared containing this group, the wave numbers of the absorption bands are  $2225\text{--}2250\text{ cm}^{-1}$  (see Table IV).

#### The Carbonyl Bands of Pyridones

The infrared spectra of the pyridone compounds exhibit the typical absorption band patterns of secondary amides. The spectra of these compounds were all recorded as Nujol mulls or potassium bromide pellets so that the solid materials at least possess the keto structure typical of amides, rather than that corresponding to hydroxy pyridines. This observation is substantiated by dipole moment evidence and infrared studies by a number of workers (14-17).

Solid secondary amides have absorption band maxima in the following ranges (12): near  $3100\text{ cm}^{-1}$ ,  $1680\text{--}1630\text{ cm}^{-1}$ , and  $1570\text{--}1515\text{ cm}^{-1}$ . The wave numbers of these absorption bands are given in Table V.

#### The Carboxylic Acid Group

The carbonyl group of aryl carboxylic acids causes an absorption band in the infrared spectrum of the com-

TABLE III. BANDS TYPICAL OF CYCLOHEPTANO RING

Compound	Frequency, $\text{cm}^{-1}$	
6,7,8,9-Tetrahydro-2-chloro-5H-cyclohepta[b]pyridine	769	828
6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-2-ol	732	825
6,7,8,9-Tetrahydro-5H-cyclohepta[b]-2-pyridone-3-carboxylic acid	718	830
6,7,8,9-Tetrahydro-3-cyano-5H-cyclohepta[b]-2-pyridone	775	830
6,7,8,9-Tetrahydro-2-chloro-3-cyano-5H-cyclohepta[b]pyridine	770	833
6,7,8,9-Tetrahydro-2-methoxy-3-cyano-5H-cyclohepta[b]pyridine	763	832
6,7,8,9-Tetrahydro-2-chloro-5H-cyclohepta[b]pyridine-3-carboxylic acid	768	832
6,7,8,9-Tetrahydro-3-hydroxymethyl-5H-cyclohepta[b]pyridine hydrochloride	760	835
6,7,8,9-Tetrahydro-3-hydroxymethyl-5H-cyclohepta[b]pyridine	774	832
6,7,8,9-Tetrahydro-3-cyano-5H-cyclohepta[b]pyridine	772	840
6,7,8,9-Tetrahydro-3-carboethoxy-5H-cyclohepta[b]pyridine	765	835
6,7,8,9-Tetrahydro-3-aminomethyl-5H-cyclohepta[b]pyridine dihydrochloride	762	835
6,7,8,9-Tetrahydro-3-aminomethyl-5H-cyclohepta[b]pyridine	773	832
6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-3-carboxylic acid	777	838
6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine-3-carboxylic acid hydrochloride	757	835
Di-([6,7,8,9-tetrahydro-5H-cyclohepta(b)pyrid- $\beta$ -yl)methyl)amine hydrochloride	754	835
Di-([6,7,8,9-tetrahydro-5H-cyclohepta(b)pyrid- $\beta$ -yl)methyl)amine	762	835
Di-([6,7,8,9-tetrahydro-5H-cyclohepta(b)pyrid- $\beta$ -yl)methyl)N-nitrosamine	745	838
6,7,8,9-Tetrahydro-5H-cyclohepta[b]pyridine	767	837

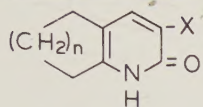


TABLE IV. NITRILE STRETCHING VIBRATIONS IN 3-CYANOPYRIDINES<sup>a</sup>

Ring System	2-Cl, 3-CN	3-CN	2-C=O, 3-CN	2-OCH <sub>3</sub> , 3-CN
Cyclopenteno	2240	2230	2225	2225
Cyclohexeno	2250	2240	2225	2226
Cyclohepteno	2250	2240	2225	2225

<sup>a</sup> Absorption bands in cm<sup>-1</sup>

TABLE V. THE N—H AND C=O STRETCHING AND N—H DEFORMATION VIBRATIONS IN PYRIDONES



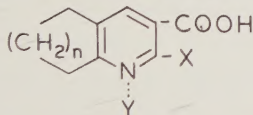
n	X	Absorption bands, cm <sup>-1</sup>		
1	—	3100	1668	1490
2	—	3140	1670	1479
3	—	3120	1663	1475
1	—COOH	3140	1660	1495
2	—COOH	3150	1669	1488
3	—COOH	3140	1640	1490
1	—CN	3150	1654	1500
2	—CN	3150	1650	1490
3	—CN	3130	1640	1483

pound in the range 1700-1680 cm<sup>-1</sup>. The substituted nicotinic acids of the three series of compounds studied here have absorption bands at appreciably higher wave numbers than those quoted for aryl acids and fall rather, in the range usually given for saturated aliphatic acids, (1725-1700 cm<sup>-1</sup>) or aryl acids heavily substituted by electronegative groups. These nicotinic acids absorb in the range 1732-1705 cm<sup>-1</sup>. Nicotinic and isonicotinic acids have carbonyl absorption bands at 1710 cm<sup>-1</sup>. These absorption bands are listed in Table VI.

#### The Ester Carbonyl Group

The carbonyl group of the ethyl esters of the substituted nicotinic acids whose spectra are included here gives

TABLE VI. THE C=O STRETCHING VIBRATION IN NICOTINIC ACIDS<sup>a</sup>



		n		
X	Y	1	2	3
Cl	—	1732	1731	1730
—	—	1720	1720	1722
OH	—	1720	1726	1705
—	HCl	1715	1720	1723

<sup>a</sup> Absorption bands in cm<sup>-1</sup>

TABLE VII. THE C=O AND C—O STRETCHING VIBRATIONS OF NICOTINIC ACID ESTERS

Compound	Absorption bands, cm <sup>-1</sup>		
6,7,8,9-Tetrahydro-3-carboethoxy-quinoline	1735	1300	1110
6,7-Dihydro-3-carboethoxy-1,5-pyridine	1730	1298	1112
6,7,8,9-Tetrahydro-3-carboethoxy-5-cycloheptal[b]pyridine	1732	1300	1110

rise to absorption bands at 1735-1730 cm<sup>-1</sup>. This wave number is high for normal aryl esters but corresponds to the position of the carbonyl absorption found in the spectra of the *o*-, *m*-, and *p*-nitrobenzoates (1733 cm<sup>-1</sup>). The nitrogen in the ring therefore has about the same effect on the position of the absorption band as a nitro group attached to a benzene ring. The CO stretching vibrations appear near 1300 and 1110 cm<sup>-1</sup> for the above compounds. These bands correspond to the C—O stretching vibration frequencies found in benzoates. These bands are given in Table VII.

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Submitted November 3, 1959, revision received January 28, 1961





# The Spectrographic Determination of Uranium 235. Part III. Use of a Multiple Hollow Cathode Source Assembly and a 22 Foot Direct Reading Eagle Spectrograph†

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## Abstract

This report, the third of a series dealing with the isotopic analysis of uranium, describes the work done with a 22-ft Eagle mounted, direct-reading spectrograph using 5 in. of a 15,000 lines/in. concave grating in the second order. The samples were excited in a multiple source assembly consisting of 4 hollow cathode source lamps and an automatically positioned selector mirror. This arrangement allowed close comparison of unknown and standard, minimized the effect of exit slit misalignment, and allowed large number of routine samples to be handled economically. A complete analysis in duplicate, including comparison standards, was made in less than 20 min.

Measurements on 4 standards having  $U^{235}$  concentrations between 10 and 51% showed average external and internal precisions of  $\pm 0.23\%$  and  $\pm 0.048\%$   $U^{235}$  for a single cathode determination. Analyses of 32 unknown samples containing 10-85%  $U^{235}$  determined independently on the optical spectrograph and the mass spectrometer, showed good agreement. Comparative measurements on 65 unknown samples in the range of 30-40%  $U^{235}$  showed an agreement of  $\pm 0.17\%$   $U^{235}$  with no significant bias. All precisions were expressed at the 95% confidence level. The factor limiting the precision—a weak line interfering with the  $U^{235}$  measurement, and the effect of  $U^{234}$  and  $U^{236}$  on the analysis are discussed.

## Introduction

This report, the third of a related series dealing with the development of a procedure for the isotopic analysis of uranium, describes the work done with a multiple, hollow-cathode source assembly and a 22-ft, direct-reading Eagle spectrograph. The results obtained with dc arc excitation and photographic recording using a Jarrell-Ash Wadsworth spectrograph were described in the first paper of this series (1). Work by other investigators was also cited in that report. With the Jarrell-Ash Wadsworth spectrograph using a direct-reading attachment and a hollow cathode source described in the second paper of this series (2), a five-fold improvement in the precision was obtained.

The present effort attempts to overcome limitations defined previously: exit slit misalignment, low percentage of time spent on the peaks, and loss of time required for the intensity to build up in the source. The work was aimed at determining the best precision possible with the available grating, although better precision would be expected with gratings of higher resolution and dispersion. The results were directly compared with mass spectrometer analyses over the range, 10-85%  $U^{235}$ . A limited examination in the vicinity of naturally occurring uranium was also made. The equipment and the method, the effect of  $U^{234}$  and  $U^{236}$  on the analysis, and the results obtained are presented.

## Equipment

The equipment consisted of three major units: the multiple hollow-cathode source assembly, the 22-ft Eagle spectrograph, and the measuring system, as shown in Figure 1.

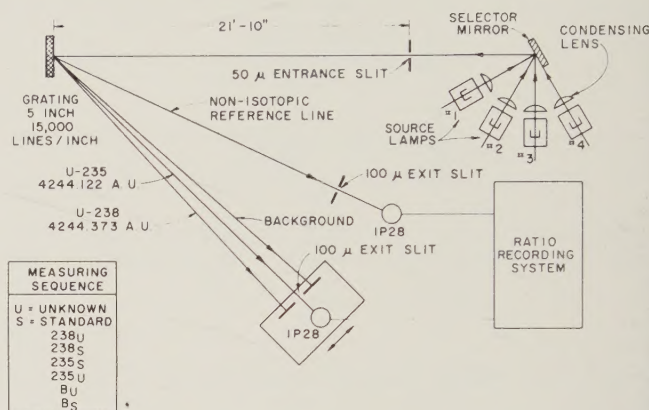


FIG. 1. DIRECT READING SPECTROGRAPH

## Multiple Source Assembly

The multiple source assembly consisted of four hollow cathode discharge lamps and a selector mirror to direct the radiation from any source lamp to the entrance slit of the spectrograph (Figure 1). The source lamps were arranged along the circumference of a circle with the mirror at the center. The mirror was located on the optic axis of the spectrograph. A separate 13.4 cm spherical condensing lens for each source formed an enlarged image of the cathode at the entrance slit of the spectrograph. The distance from the cathode to the entrance slit of the spectrograph, by way of the selector mirror, was 135 cm.

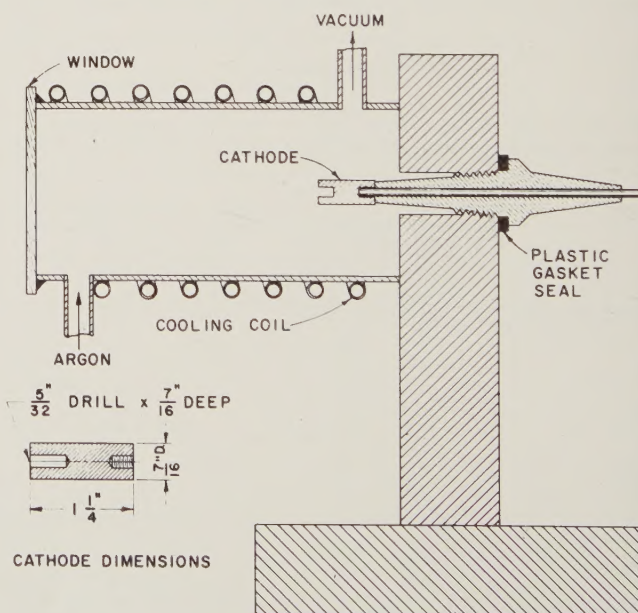


FIG. 2. HOLLOW CATHODE SOURCE

†This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.



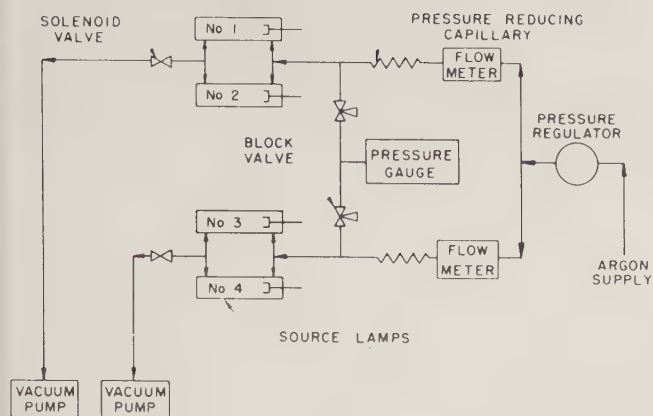


FIG. 3. MANIFOLD SYSTEM FOR ARGON FLOW

The design of the hollow cathode source lamp is shown in Figure 2. The lamp, similar to the hot-cathode type previously described (2), was rigidly mounted on a heavy support and retained the sample-change feature using a screw-in insulator. With the exception of the window, it used an all-metal envelope and required only one wax joint. The argon support-gas manifold system (Figure 3) was designed for the lamps to be operated in groups of two. The support gas, after passing through the source, was exhausted to the atmosphere through a pump. Each of the 4 source units were excited by an independent constant-current power supply.

A servo-drive, Figure 4, controlled with a four-point selector switch, rapidly and precisely positioned the mirror. A projection system, consisting of a projection lamp, an auxiliary mirror mounted on the same shaft as the main mirror, and four targets on the wall, provided a convenient check for the positioning of the source selector mirror.

### Spectrograph

A 22-ft, direct-reading Eagle spectrograph (3), with a 15,000 line/in. concave grating ruled over a 5-in. surface, was used in the second order to provide a theoretical resolution of 150,000 and an inverse linear dispersion of 1.33 Å/mm. The grating was blazed for the 1st and 2nd order of the visible spectrum. No optical filters were employed, since tests with such filters indicated essentially no interference from higher or lower orders.

The spectrograph possessing experimental flexibility and mechanical stability was specifically designed for development of direct-reading spectrographic techniques. The in-

strument was assembled in an insulated room whose temperature was controlled with a resistance thermometer to  $\pm 0.1^\circ\text{C}$ . This temperature control corresponds to  $\pm 0.0035$  Å at 4244 Å, or  $\pm 2.6$  microns in the position of the dispersed spectrum. The same shift is also produced by a change of only 2 mm Hg in barometric pressure, which was the principal cause of exit-slit drift. To minimize drift effects on the analysis, a measuring sequence was devised to compare unknown with standard under identical exit-slit alignment conditions.

### Measuring System

The measuring system, which was a modification of the scanning technique developed by Crosswhite (4) and Dieke (5), included two exit-slit, photomultiplier-tube combinations (1P21 and 1P28 photomultiplier tubes were used interchangeably). One combination, mounted on a carriage, was driven sequentially to each of three positions to measure, respectively, the intensities of the  $\text{U}^{235}$  line at 4244.122 Å, the  $\text{U}^{238}$  line at 4244.373 Å, and the background at 4244.0 Å. This positioning was made quickly and precisely with a servo-drive controlled by a three point selector switch similar to the drive shown in Figure 4 for the source selector mirror.

The second exit slit and photomultiplier tube was fixed in position to measure the intensity of the non-isotopic uranium line at 3890.364 Å. The signal from the first photomultiplier tube was measured as a ratio to the signal from the second photomultiplier tube by passing the signal currents through polystyrene capacitors for a specific time or through high value resistors and measuring the ratio of the voltages across the capacitors or resistors with a ratio recorder. Measuring the  $\text{U}^{235}$ ,  $\text{U}^{238}$ , and background relative to the non-isotopic uranium reference line minimized the effect of drift in source intensity during the short time (about 1 min) required to measure the two isotopic lines and the background (see relationship under "Calculations"). The precision was the same with either resistors or capacitors in the anode circuits. The resistors allowed observing the measurement as it progressed. The integrating capacitors were particularly useful for large numbers of routine samples, since they provided averaged values and could be adapted to readout systems.

The high voltage for both photomultiplier tubes was obtained from a common power supply to minimize the effect of voltage fluctuations. The circuitry for the amplifiers, power supplies, and ratio recorder was described previously (3).

### Method

The method for isotopic analysis of uranium is described in three parts: sample preparation and excitation, the measuring sequence, and calculations.

### Sample Preparation and Excitation

The sample consisting of 50 mg of  $\text{U}_3\text{O}_8$  was dissolved in one drop of nitric acid in a glass test tube. The excess acid was driven off by heating, and the remaining uranyl nitrate was dissolved in one drop of water. The solution was then transferred to an iron cathode, evaporated to dryness, and ignited to convert the uranyl nitrate to an adhering deposit of  $\text{U}_3\text{O}_8$ . After cooling, the cathode cavity was brushed lightly with a length of pipe cleaner to remove any loose particles, which could cause instability in the discharge. This cathode and a cathode containing a standard sample, identically prepared, were inserted in a pair of source lamps. The lamps were operated in a con-

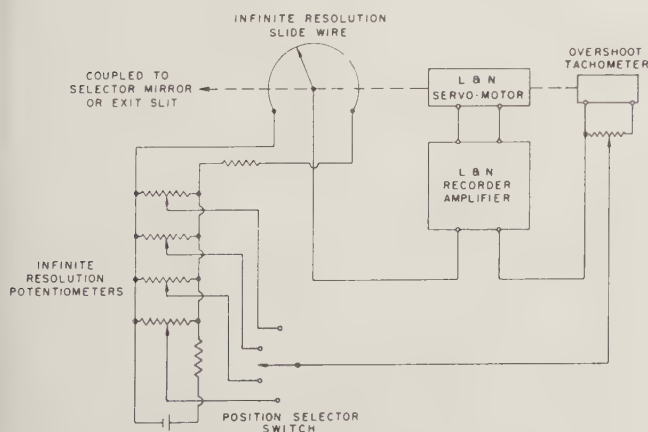


FIG. 4. BASIC SERVO-DRIVE CIRCUIT



tinuously flowing atmosphere of argon\* at 6 mm Hg absolute, and excited at 300 ma.

Since the precision of a photoelectric measurement increases with the square root of the signal current (4, 5), the sample size and source excitation current were selected to produce maximum spectrum intensity. For any specified current level, the intensity of the spectrum reached a maximum with a specific sample size; further increase in sample size did not result in greater intensity. The 50 mg sample size was selected on this basis for an excitation current of 300 ma. Although no inherent limit for the excitation current was observed, a number of practical limitations, such as maximum safe operating temperature of the source, capacity of the power supply, and available sample size on a routine basis, dictated a maximum excitation current of 300 ma.

### Measuring Procedure

The measuring sequence was designed to measure the unknown and comparison standard in a pair of lamps under as nearly identical conditions as practical. Several sequences were possible with each sequence placing the burden of precision on a different part of the system. The sequence shown in Figure 1 minimized the effect of exit slit misalignment and retained a close comparison of unknown and standard, since the unknown and standard would be affected similarly.

The sequence was started with the exit slit and source selector mirror positioned to measure the  $U^{238}$  intensity of the unknown. Without disturbing the exit slit, the source selector mirror was then positioned to measure the  $U^{238}$  intensity of the standard. The  $U^{235}$  intensity of the standard was then measured by positioning the exit slit over the  $U^{235}$  line. The mirror was then positioned (again without disturbing the exit slit) to measure the  $U^{235}$  intensity of the unknown. The sequence was completed by positioning the exit slit to measure the background, and positioning the source selector mirror, first for the unknown sample and then for the standard. The background was measured to the low wavelength side of the  $U^{235}$  line to provide a correction for the general case where  $U^{235}$  required the more accurate correction and where sufficient resolution was not available to measure background between the isotopic lines. The exit slit and mirror were left in each of the six positions of the sequence for 10 sec. Since about 2 sec was required to move to the next position of the sequence, a high percentage of the measuring time, in contrast to conventional scanning, was spent on the peaks. Figure 5 is a recording showing the measurement of  $U^{235}$ ,  $U^{238}$  and the background correction. As stated earlier, all recorded measurements were made relative to a non-isotopic uranium reference line, measured continuously throughout the sequence. The entire sequence, which required about 1 min, was repeated 10 times for the analysis of each cathode.

Duplicate cathodes were prepared for each unknown and standard. The duplicate measurement was made in the same pair of lamps, but with the unknown and standard reversed to cancel minor differences between the 2 lamps. Thus the entire measuring procedure for an unknown sample required 20 min.

While measurements were in progress with the first pair of lamps, a second unknown and standard were pre-

\*It was reported earlier (2) that maximum intensity was obtained with a 9:1 (mole) mixture of argon to helium. Similar intensity tests made in the present work indicated maximum intensity with "pure" argon. The reasons for this difference are not known, since the conditions were not identically reproduced.

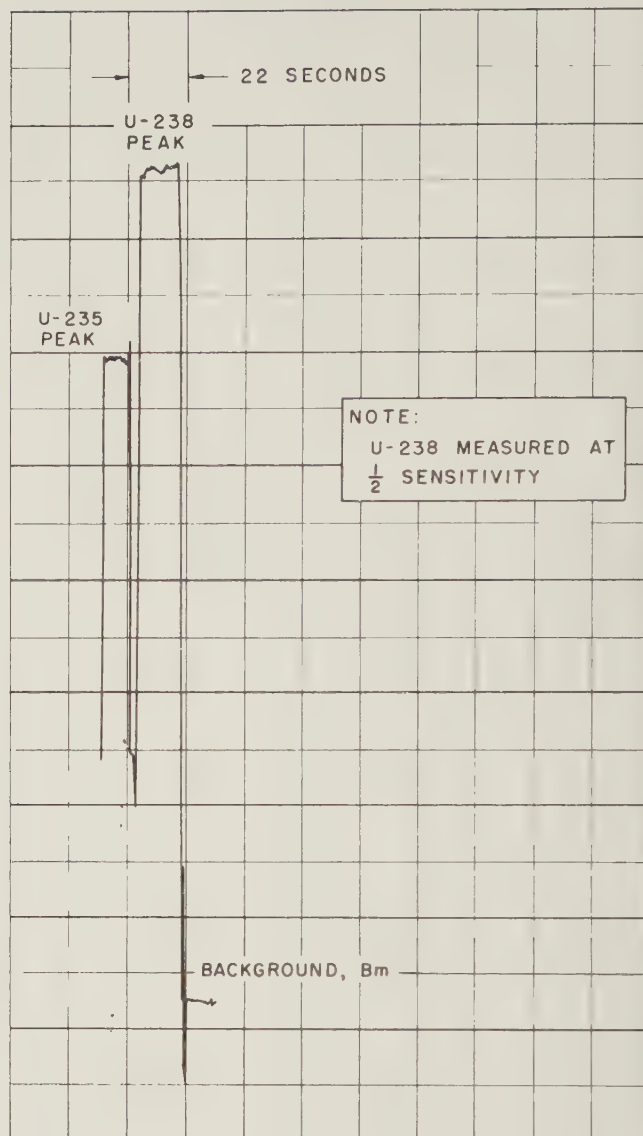


FIG. 5. RECORDING OF  $U^{235}$ ,  $U^{238}$ , AND BACKGROUND AT 26 %  $U^{235}$  CONCENTRATION

burning in the second pair of lamps. This arrangement overcame the loss of time due to the 15-20 min pre-burn period (2).

### Calculations

The intensity ratio,  $I_{U^{235}}/I_{U^{238}}$ , was calculated from the 3 measured intensity ratios for the unknown and the standard using the following relationship:

$$\frac{\left(\frac{I_{U^{235}} + Bu}{I_{Ref.}}\right) - \left(\frac{I_{Bm}}{I_{Ref.}}\right)}{\left(\frac{I_{U^{238}} + Bu}{I_{Ref.}}\right) - \left(\frac{I_{Bm}}{I_{Ref.}}\right)} = \frac{I_{U^{235}}}{I_{U^{238}}} = R$$

where the first terms in the numerator and denominator are the measured intensity ratios of the  $U^{235}$  and  $U^{238}$  lines (including underlying background, Bu), to the intensity of the non-isotopic uranium reference line.  $I_{Bm}$  is the background correction measured as a ratio to the reference line. The background under the  $U^{235}$  line and under the  $U^{238}$  line were assumed equal to the measured background, Bm. This assumption was not strictly valid, but the error was minimized, since the calculations for the



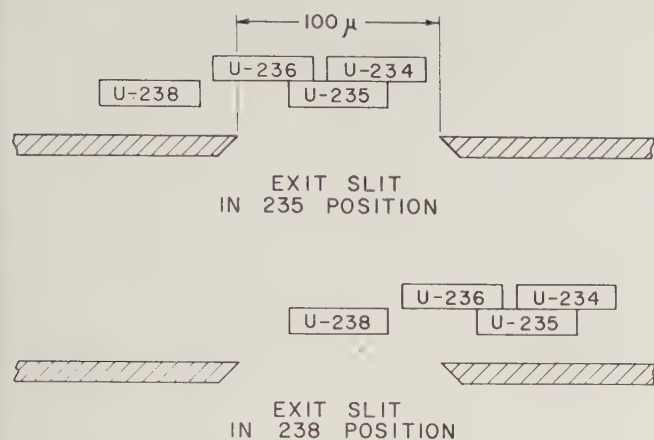


FIG. 6. RELATIVE POSITION OF LINES AND SLITS

unknown and for the standard were made in the same manner.

The intensity ratios were converted to measured %  $U^{235}$  using the following relationship:

$$(R/R+1) 100 = \text{Measured } \% U^{235}$$

The difference between the known and the measured values for  $U^{235}$  in the standard was applied as a correction to the measured %  $U^{235}$  of the unknown to obtain the corrected %  $U^{235}$  of the unknown.

#### Minor Isotopes

$U^{234}$  and  $U^{236}$ , present up to a few %, are referred to as minor isotopes. Figure 6 (drawn to scale) shows the distribution of the isotopes in the spectrum based on geometric optics for a  $50\mu$  entrance slit and a  $100\mu$  exit slit. Interferences due to minor isotopes were calculated from the known slit widths and the inverse linear dispersion of  $0.00133 \text{ \AA}/\mu$ . Seventy-four % of the  $U^{236}$  intensity ( $4244.226 \text{ \AA}$ ) and 100% of the  $U^{234}$  intensity ( $4244.075 \text{ \AA}$ ) would pass through the exit slit when positioned over the  $U^{235}$  line ( $4244.122 \text{ \AA}$ ) and hence would be added to the  $U^{235}$  intensity measurement. With the exit slit positioned over the  $U^{238}$  line ( $4244.373 \text{ \AA}$ ), 37% of the  $U^{236}$  intensity would be added to the  $U^{238}$  intensity measurement. These calculated intensity distributions were confirmed by comparative measurement of a standard and a sample prepared by adding known quantities of  $U^{234}$  and  $U^{236}$ .

Unless the  $U^{234}$  and  $U^{236}$  concentrations were the same in the standard and the unknown, either 1) a correction would have to be applied for the  $U^{234}$  and  $U^{236}$  concentration differences between the standard and unknown based on an analysis of  $U^{234}$  and  $U^{236}$  by independent means, or 2) a spectrograph with sufficient resolution to separate the  $U^{234}$  lines and the  $U^{236}$  from the  $U^{235}$  lines would have to be used, if unbiased results are to be obtained.

For this evaluation, the concentration of  $U^{234}$  and  $U^{236}$  were known for samples above 58%  $U^{235}$  and corrections for the minor isotopes were made in calculating the optically measured values.

#### Results

The precision was evaluated at the higher concentrations of  $U^{235}$  in two ways: by comparing the optical spectrographic measurements with mass spectrometer measurements on a large number of unknown samples, and by repeat measurements on isotopic uranium standards. A

TABLE I. COMPARISON OF OPTICAL AND MASS SPECTROMETER ANALYSES OF UNKNOWN SAMPLES, %  $U^{235}$ 

Optical Spectrometer	Mass Spectrometer	Difference
10.25	10.36	-0.11
11.86	12.00	-0.14
13.70	13.75	-0.05
14.51	14.60	-0.09
15.79	15.78	+0.01
16.62	16.70	-0.08
19.45	19.50	-0.05
23.12	23.13	-0.01
23.28	23.29	-0.01
24.69	24.76	-0.10
32.63	32.74	-0.11
37.90	37.85	+0.05
42.26	42.18	+0.08
44.18	44.27	-0.09
46.73	46.73	0.00
49.27	49.39	-0.12
52.08	52.10	-0.02
55.99	56.09	-0.10
56.59	56.56	+0.03
58.68	58.61	+0.07
61.20	61.26	-0.06
64.45	64.34	+0.11
67.20	66.90	+0.30
70.10	69.81	+0.29
72.76	72.38	+0.38
73.12	72.84	+0.28
75.11	75.09	+0.02
77.73	77.38	+0.35
79.96	79.78	+0.18
82.08	81.73	+0.35
84.18	84.14	+0.04
85.09	85.13	-0.04

limited examination in the vicinity of naturally occurring uranium was also made.

#### Comparison of Optical and Mass Spectrometer Data

Table I shows the results of 32 unknown samples from 10%—85%  $U^{235}$  determined independently on the optical spectrometer and the mass spectrometer. The optical values were obtained with the multiple hollow cathode source assembly (see *Method*). The differences between the two methods are shown in column 3.

To determine the agreement between the 2 methods and whether any significant bias exists, measurements were made on 65 unknown samples in the region 30—40%  $U^{235}$  and were compared with mass spectrometer measurements made on the same samples. The paired values agreed to within 0.17%  $U^{235}$  for a single comparison with no significant bias (calculated at the 95% confidence level).

#### Repeat Measurements on Isotopic Standards

For this part of the evaluation, a single hollow cathode source lamp was used. Hence this series of measurements was made without the benefit of comparing unknowns and standards in a pair of source lamps under identical exit-slit alignment conditions. Constant checking and realigning of the exit slit was necessary during the measurements to prevent impairing the precision. Ten samples or cathodes were prepared for each of four isotopic standards at the 10, 15, 26, and 51%  $U^{235}$  levels. Ten repeat scans were made on each cathode. The external and internal precisions (calculated at the 95% confidence level) are given in Table II on an absolute and on a relative basis for each of the 4 standards. The external (cathode-to-cathode) precision is expressed for a single cathode analysis (average of 10 scans). The internal precision (for repeat scans on the same cathode) is expressed for an average of 10 scans on that cathode. Since the internal and external precisions



TABLE II. PRECISIONS OF REPEAT MEASUREMENTS

% U <sup>235</sup>	External Precisions (Cathode to Cathode)		Internal Precisions (Repeat Scans on Same Cathode)	
	Absolute (% U <sup>235</sup> )	Relative (% of Value)	Absolute (% U <sup>235</sup> )	Relative (% of Value)
10.15	±0.23	±2.24	±0.044	±0.43
15.36	±0.30	±1.97	±0.052	±0.34
25.57	±0.16	±0.61	±0.043	±0.17
50.74	±0.23	±0.45	±0.051	±0.10
Av. = ±0.23			Av. = ±0.048	

were both expressed for an average of 10 repeat scans on the cathode, the external and internal precisions may be directly compared. The differences are believed to be primarily due to a weak interfering uranium line at approximately 4244.09 Å that is not resolved from the U<sup>235</sup> line at 4244.122 Å. This interfering line, which shows excitation behavior different from either the two isotopic lines or the measured background, is apparently the erratic factor limiting the precision. Evidence for this line will be given in the following section.

#### Examination of Naturally Occurring Uranium

Exploratory study at the level of naturally occurring uranium (0.7115% U<sup>235</sup>) revealed a weak interfering line not resolved from the U<sup>235</sup> line. Recordings of the spectrum in the vicinity of the U<sup>235</sup> line for highly depleted uranium (0.031% U<sup>235</sup>) and for naturally occurring uranium are shown in Figure 7. For the highly depleted uranium, a relatively strong, symmetrical structure was seen at the U<sup>235</sup> position. At the level of naturally occurring uranium, the recorded structure was unsymmetrical and showed no change in intensity, although the concentration of U<sup>235</sup> was increased over twenty fold. Recordings at higher concentrations of U<sup>235</sup> indicated that the interfering line at approximately 4244.09 Å was unresolved from the U<sup>235</sup> line at 4244.122 Å. Hence at the level of naturally occurring uranium, most of the measured intensity at the U<sup>235</sup> position arises from the interfering line, and no acceptable analytical data were collected at that level. For this examination, a 25μ exit slit and a 50μ entrance slit were used. Somewhat better resolution, at the expense of intensity, might be realized with narrower slits. As stated earlier, this interfering line is believed to be a uranium line showing excitation behavior different from the isotopic uranium lines at 4244 Å or the measured background. The interference may possibly be suppressed by changing the excitation conditions, or eliminated if an isotopic line pair free from such interference could be found at another wavelength.

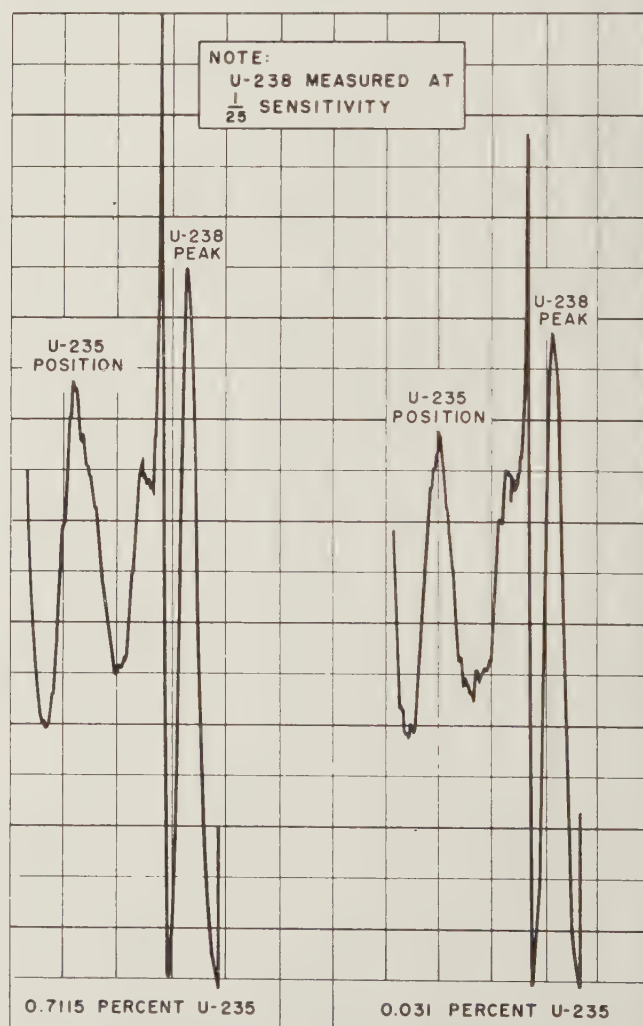
#### Discussion and Summary

Certain limitations previously experienced were overcome with a new measuring technique using a multiple hollow-cathode source assembly. A high percentage of the measuring time was spent on the peaks in contrast to conventional scanning. The effect of exit slit misalignment was minimized by measuring each unknown with a comparison standard in a pair of source lamps under as nearly identical conditions as possible. The loss of time due to the 15–20 min pre-burn period was overcome with the multiple hollow-cathode source assembly, which allowed pre-burning one sample while measurements were in progress on another sample. These techniques may be used with any well-constructed spectrograph of equivalent or higher resolution and dispersion.

Measurements on 4 standards having U<sup>235</sup> concentrations of 10.15, 15.36, 25.57, and 50.74% showed an average sample-to-sample precision of ±0.23% U<sup>235</sup> for a single cathode determination. The average internal precision represented a three-fold improvement over that reported earlier in this series (2). No external (sample-to-sample) precision data were available for that period.

Measurements on 32 unknown samples of 10–85% U<sup>235</sup> determined independently on the optical spectrograph and the mass spectrometer showed good agreement. Measurements on 65 unknown samples in the region, 30–40% U<sup>235</sup> also determined independently on the optical spectrograph and mass spectrometer, showed an agreement within 0.17% U<sup>235</sup> and no significant bias between the 2 methods. This figure includes the mass spectrometer variance. All precisions were expressed at the 95% confidence level.

Several limitations remain. A weak interfering line, believed to be a uranium-line, interferes with the U<sup>235</sup> measurements. At low U<sup>235</sup> concentrations, this interference is relatively large. The interference may possibly be suppressed by changing the excitation conditions, or eliminated if a line pair free from such interference could

FIG. 7. INTERFERENCE WITH THE U<sup>235</sup> MEASUREMENTS



be found at another wavelength.  $U^{234}$  and  $U^{236}$  were not resolved from the  $U^{234}$  line and will contribute errors to the extent that the concentration of these isotopes differ in unknown and standard. Greater resolution would be needed to separate these interferences.

The sample preparation described is a time-consuming process not always resulting in the desired smooth adhering deposit of the sample in the cathode cavity. A simpler, more dependable method for sample preparation is needed.

#### Literature Cited

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Submitted January 7, 1960

## X-ray Powder Diffraction Data for 2,4-Dinitrophenylhydrazones of Aldehydes and Ketones\*†

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### Abstract

In order to extend the data available for the identification of carbonyl compounds, the x-ray powder diffraction patterns of sixty-four 2,4-dinitrophenylhydrazones of aldehydes and ketones were determined. An alphabetical table includes 39 additional compounds found in the literature. A second numerical table indexes the spacing and intensities of the three strongest lines in Hanawalt groups. The complete new diffraction pattern data are available from the American Documentation Institute.

Aldehydes and ketones are frequently identified as their 2,4-dinitrophenylhydrazone (DNPH) derivatives because these are readily prepared, even from mg quantities of starting material. The relatively high melting points of the DNPH's are their most commonly used means of identification (1), but other physical properties have also been used e.g., optical properties (2,3), chromatographic properties (4,5), visible and ultraviolet absorption spectra (6,7), and infrared spectra (8). The DNPH's have also been used successfully for the quantitative determination of pure and mixed carbonyl compounds (9-14). The satisfactory identification of DNPH's by one or other of these methods is sometimes difficult due to the presence of polymorphs or geometrical isomers (2,9,10,15-17). Occasionally impurities form constant melting point mixtures (2,18). Difficulties owing to side reactions, mixed-crystal formation, and structural rearrangements have been encountered (2,19).

The x-ray powder diffraction method is very suitable for identifying polymorphs, geometrical isomers, and mixed crystals. It can be applied to very small amounts of material, to impure samples, or directly to mixtures (9,10,18,20,21). For example, two samples of *m*-nitrobenzaldehyde DNPH, with m.p.'s of 292° and 252-4°C respectively, gave the same x-ray diffraction pattern and were readily and unambiguously identified although one sample was evidently impure. It is worth noting that while the measurements of the diffraction lines on the film of an unknown serve as an excellent basis for identi-

fication, often, because of impurities or abnormalities, it is desirable to make a direct comparison with the pattern obtained from an authenticated sample. In some cases the use of another physical method may serve to prevent premature identification.

The present work was designed to extend the x-ray data already available for carbonyl DNPH's (2,9,10,12,20,22). Table I is an alphabetical list of the parent aldehydes and ketones which were examined. It also includes 39 compounds described in the literature. The Roman numerals assigned to the various forms are the same as those assigned by previous workers (9,10,12).

The three strongest lines and their intensities are arranged in Hanawalt groups in Table II. Malkin (21) listed only a few *d* values as very strong, strong, or medium; where he has given more than three *d* values as equally strong, the three largest *d* values are listed. The data given for *n*-propionaldehyde DNPH *Form I* agree well with the partial data of Clark (9), Gordon (10), and Mitchell (12) but do not agree with Malkin's data (21). Malkin's sample appears to be a mixture of *Form I* and *II*.

The complete pattern data on the 64 aldehyde and ketone DNPH's and 3 mononitrophenylhydrazones have been deposited with the American Documentation Institute from whom copies may be ordered if desired.†

### Experimental

The specimens were first checked for phase purity under a binocular polarising microscope and impure specimens rejected. Some samples of uniform colour contained crystals of different habits. Crystals of each habit were mechanically separated and separately photographed to confirm their identity. In some cases the different habits corresponded to different polymorphs. In cases where any doubt arose a chemical analysis was carried out, and such specimens were included only if authenticated. The resulting x-ray diffraction patterns were all checked for the possible presence of 2,4-dinitrophenylhydrazine which has been found as an impurity in DNPH's. Whenever possible, the patterns were compared with the partial data in the literature.

\*Issued as N.R.C. No. 6246

†For supplementary material, order Document 6532 from the Chief, Photoduplication Service, Library of Congress, Washington 25, D.C. Auxiliary Publication Project, remitting \$2.00 for microfilm (35 mm) or \$3.75 for photocopies.

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TABLE I. ALPHABETICAL INDEX OF COMPOUNDS

2,4-Dinitrophenyl- hydrazone of	Empirical formula	<i>d</i> strongest line
Acetaldehyde, <i>Form I</i>	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> N <sub>4</sub>	9.4
Acetaldehyde, <i>Form II</i>	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> N <sub>4</sub>	9.2
Acetone, <i>Form I</i>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	3.26
Acetone, <i>Form II</i>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	9.5
Acetophenone	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.34
<i>p</i> -Cl-Acetophenone	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> N <sub>4</sub> Cl	3.30
1-Acetylcyclohexene	C <sub>14</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	6.1
9,10-Anthraquinone, 2-methyl-	C <sub>21</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	8.5
Benzalacetone	C <sub>14</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.36
Benzalacetophenone	C <sub>21</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	3.48
Benzaldehyde	C <sub>13</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	3.31
Benzaldehyde, <i>m</i> -nitro	C <sub>13</sub> H <sub>9</sub> O <sub>6</sub> N <sub>5</sub>	3.16
Benzil	C <sub>20</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.64
Benzophenone	C <sub>19</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	4.46
Butanal, 2,2-dimethyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	11.7
Butanal, 2-ethyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	12.3
Butanal, 2-methyl-2-ethyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	13.4
Butanal, 2,3,3-trimethyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	12.0
2-Butanone, <i>Form I</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	12.5
2-Butanone, <i>Form II</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	12.1
2-Butanone, 3,3-dimethyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	7.3
2-Butanone, 3-methyl-	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.30
3-Butene-2-one, 3-ethyl-	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.34
1-Butene-3-one, 2-methyl-	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	9.0
<i>iso</i> -Butyraldehyde, <i>Form I</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	12.4
<i>iso</i> -Butyraldehyde, <i>Form II</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	11.7
<i>n</i> -Butyraldehyde, <i>Form I</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	13.4
<i>n</i> -Butyraldehyde, <i>Form II</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	11.7
<i>n</i> -Butyraldehyde, <i>Form III</i>	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	12.6
Butyrophenone	C <sub>16</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	3.52
<i>d</i> -Camphor	C <sub>16</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	5.21
Cinnamaldehyde	C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.36
<i>d</i> l-Citral	C <sub>16</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	4.48
Crotonaldehyde	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	3.25
Cyclohexanone	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	11.5
Cyclopentanone	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	11.1
Cyclopentanone, 3-cyclo-pentylidene	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	3.40
Cyclopentanone, $\alpha$ -methyl-	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.46
Cyclopentanone, $\beta$ -methyl-	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	11.0
<i>n</i> -Decanal	C <sub>16</sub> H <sub>24</sub> O <sub>4</sub> N <sub>4</sub>	4.72
Dibenzalacetone	C <sub>23</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	3.24
Difurfurylidene acetone	C <sub>18</sub> H <sub>14</sub> O <sub>6</sub> N <sub>4</sub>	3.37
<i>n</i> -Dodecanal	C <sub>18</sub> H <sub>28</sub> O <sub>4</sub> N <sub>4</sub>	4.73
Formaldehyde	C <sub>7</sub> H <sub>6</sub> O <sub>4</sub> N <sub>4</sub>	10.4
<i>d</i> -Fructose dioxane solvate	C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> • C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	3.87
Furfuraldehyde, <i>Form I</i>	C <sub>11</sub> H <sub>8</sub> O <sub>5</sub> N <sub>4</sub>	3.17
Furfuraldehyde, <i>Form II</i>	C <sub>11</sub> H <sub>8</sub> O <sub>5</sub> N <sub>4</sub>	3.24
Furfuraldehyde, <i>Form III</i>	C <sub>11</sub> H <sub>8</sub> O <sub>5</sub> N <sub>4</sub>	3.26
Furfurylidene acetone	C <sub>14</sub> H <sub>12</sub> O <sub>5</sub> N <sub>4</sub>	3.40
2,6-Heptadione, 4-methyl-	C <sub>13</sub> H <sub>18</sub> O <sub>5</sub> N <sub>4</sub>	3.40
<i>n</i> -Heptanal	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	4.63
2-Heptanone	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	13.2
4-Heptanone	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	14.9
4-Heptanone, 2,6-dimethyl-	C <sub>15</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	3.71
1-Heptanone, 1-phenyl-	C <sub>20</sub> H <sub>24</sub> O <sub>4</sub> N <sub>4</sub>	3.37
3-Heptene-2-one, 4,6,6-trimethyl-	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	3.15
1-Hexadecanone, 1-phenyl-	C <sub>28</sub> H <sub>40</sub> O <sub>4</sub> N <sub>4</sub>	4.25
<i>n</i> -Hexanal	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	15.5
2-Hexanone	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	12.8
3-Hexanone, 2-methyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	13.6
4-Hexene-2-one, 3,4-dimethyl-, <i>Form I</i>	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	3.20
4-Hexene-2-one, 3,4-dimethyl-, <i>Form II</i>	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	3.27
5-Hexene-3-one, 4,4,5-trimethyl-	C <sub>15</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	3.45
1-Naphthaldehyde, potassium-aci-5-nitro-	C <sub>17</sub> H <sub>10</sub> O <sub>6</sub> N <sub>5</sub> K	3.44
1-Naphthyl methyl ketone, potassium-aci-5-nitro-	C <sub>18</sub> H <sub>12</sub> O <sub>6</sub> N <sub>5</sub> K	8.2
1-Naphthyl tetradecyl ketone, potassium-aci-5-nitro-	C <sub>21</sub> H <sub>38</sub> O <sub>6</sub> N <sub>5</sub> K	9.1
<i>n</i> -Nonanal	C <sub>15</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	4.72
<i>n</i> -Octanal	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	4.58
2-Octanone, <i>Form I</i>	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	3.75
2-Octanone, <i>Form II</i>	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	3.34

TABLE 1. (Cont'd)

2,4-Dinitrophenyl- hydrazone of	Empirical formula	<i>d</i> strongest line
Pentanal, 4-methyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	11.5
2-Pentanone	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.61
3-Pentanone	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	12.60
2-Pentanone, 3,4-dimethyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	3.29
2-Pentanone, 4,4-dimethyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	11.5
3-Pentanone, 2,4-dimethyl-	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	13.7
2-Pentanone, 4-methyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	13.7
3-Pentanone, 2-methyl-	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	7.0
2-Pentanone, 3,3,4,4-tetramethyl-	C <sub>15</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	13.9
2-Pentanone, 3,3,4-trimethyl-	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	3.33
2-Pentanone, 3,4,4-trimethyl-	C <sub>14</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	8.0
3-Pentene-2-one, 3,4-dimethyl-	C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	12.3
4-Pentene-2-one, 3,4-dimethyl-	C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	3.18
3-Pentene-2-one, 3-ethyl- <i>Form I</i>	C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	3.48
3-Pentene-2-one, 3-ethyl- <i>Form II</i>	C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> N <sub>4</sub>	12.1
4-Pentene-2-one, 3,3,4-trimethyl	C <sub>14</sub> H <sub>18</sub> O <sub>4</sub> N <sub>4</sub>	12.3
9,10-Phenanthraquinone	C <sub>20</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.24
Phenyl acetone	C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.31
Propanal, 2,2-dimethyl-	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.35
<i>n</i> -Propionaldehyde, <i>Form I</i>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	9.6
<i>n</i> -Propionaldehyde, <i>Form II</i>	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	11.0
Propiophenone	C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.37
<i>p</i> -Quinone	C <sub>12</sub> H <sub>8</sub> O <sub>4</sub> N <sub>4</sub>	3.46
Salicylaldehyde	C <sub>13</sub> H <sub>10</sub> O <sub>4</sub> N <sub>4</sub>	3.17
<i>o</i> -homo-Salicylaldehyde	C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	7.2
<i>p</i> -homo-Salicylaldehyde	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub> N <sub>4</sub>	3.18
1-Tetradecanone, 1-phenyl-	C <sub>26</sub> H <sub>30</sub> O <sub>4</sub> N <sub>4</sub>	9.4
<i>n</i> -Tridecanal	C <sub>19</sub> H <sub>30</sub> O <sub>4</sub> N <sub>4</sub>	4.77
<i>n</i> -Undecanal	C <sub>17</sub> H <sub>26</sub> O <sub>4</sub> N <sub>4</sub>	4.75
<i>iso</i> -Valeraldehyde, <i>Form I</i>	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	12.7
<i>iso</i> -Valeraldehyde, <i>Form II</i>	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	11.8
<i>n</i> -Valeraldehyde	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> N <sub>4</sub>	3.78
Vanillin	C <sub>11</sub> H <sub>12</sub> O <sub>6</sub> N <sub>4</sub>	3.39

The samples were ground and mounted in thin-walled (0.01 mm) 0.3 mm diam. glass capillaries.† For some compounds excessive grinding produces changes in the diffraction pattern, and where such changes are suspected a second preparation, lightly crushed between a microscope cover slip and a glass slide, provides a useful check. A circular camera, 114.6 mm diam., was used. The film was mounted in the Straumanis manner. Nickel filtered Cu radiation was employed ( $\lambda K\alpha_1$  1.5405 Å) with which the largest *d* value observable was about 17 Å. The accuracy of the observed *d* values is about  $\pm 0.5$  Å for values greater than 12 Å, but this improves until in the medium *d* range the difference between independent photographs is less than 1%. Accordingly the observed *d* values were rounded off to one decimal figure for *d* > 6.0 Å and to two decimal figures for *d* < 6.0 Å. No shrinkage correction was used (23). The relative intensities (*I*/*I*<sub>1</sub>) were estimated visually using a calibrated film strip with a logarithmic scale; two independent estimates were made, and the average was taken.

#### Acknowledgement

It is a pleasure to acknowledge the help of Dr. F. W. Matthews who suggested the present work and supplied all the samples which were prepared by Prof. M. L. Willard and co-workers at Pennsylvania State College. The authors wish to thank Mrs. F. Beck, Mrs. P. Belanger, and Miss A. Graves who prepared and measured the films. They are grateful to Mr. R. H. Séguin for chemical analyses of 14 compounds and to Dr. A. O. McIntosh who kindly made independent measurements for 6 compounds.

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TABLE II. NUMERICAL INDEX OF STRONGEST LINES ARRANGED IN HANAWALT GROUPING,  
 $d_1, d_2$ , and  $d_3$  are the three strongest lines;  $d_4$  is the largest  $d$  value<sup>a</sup>.

$d_1$	$d_2$	$d_3$	$d_4$	$I_1$	$I_2$	$I_3$	$I_4$	2,4-Dinitrophenylhydrazones of:
15.9—14.0								
15.0	13.4	3.16	15.0	27*	100b	40	27*	2-Methyl-2-ethyl-butanal
14.0	7.2	3.17	14.0	75*	100	90b	75*	<i>o</i> -homo-Salicylaldehyde
15.5	3.72	3.28	15.5	100	100	80	100	<i>n</i> -Hexanal
14.9	3.44	7.8	14.9	100	56	30	100	4-Heptanone (9)
14.8	3.27	6.8	65	100	70			3,4-Dimethyl-4-hexene-2-one, Form II (20)
14.0	3.24	3.83	14.0	80*	100	65	80*	Dibenzalacetone
15.4	3.20	7.2	85	100	90			3,4-Dimethyl-4-hexene-2-one, Form I (20)
13.9—12.0								
13.9	8.5	3.68		100	100	100		3,3,4,4-Tetramethyl-2-pentanone (20)
12.5	7.8	4.23	12.5	100	90	60	100	2-Butanone, Form I (10)
12.80	7.75	3.47	12.8	100	72	56	100	2-Hexanone (9)
13.7	7.6	3.48	13.7	100	78	42	100	4-Methyl-2-pentanone (9)
12.60	7.10	3.54	12.60	100	76	37	100	3-Pentanone (9, 10)
12.3	7.0	9.1	12.3	100	65	50	100	3,3,4-Trimethyl-4-pentene-2-one
13.7	6.90	3.40	13.7	100	78	62	100	2,4-Dimethyl-3-pentanone (9)
12.7	6.5	4.28	12.7	100	80	40	100	<i>iso</i> -Valeraldehyde, Form I (10)
13.6	5.18	7.8	13.6	100*	90	65	100*	2-Methyl-3-hexanone
12.0	5.11	4.82	12.0	100	82	55	100	2,3,3-Trimethyl-butanal
12.3	4.95	3.48		100	100	100		3,4-Dimethyl-3-pentene-2-one (20)
12.5	3.61	10.6	12.5	78	100	66	78	2-Pentanone (9)
12.1	3.60	7.0		100	90	85		3-Ethyl-3-pentene-2-one, Form II (20)
12.9	3.48	7.6		85	100	85		3-Ethyl-3-pentene-2-one, Form I (20)
13.2	3.47	7.5	13.2	100	70	48	100	2-Heptanone (9)
13.8	3.40	5.34	13.8	75*	100	75	75*	3-Cyclopentylidene-cyclopentanone
12.4	3.35	5.34	12.4	60*	100	55	60*	2,2-Dimethyl-propanal
12.8	3.34	7.8	17.0	75	100	40	20*	2-Octanone, Form II
12.3	3.30	7.2	12.3	90*	100	90	90*	3-Methyl-2-butanone
12.6	3.28	4.33	12.6	100	83	26	100	<i>n</i> -Butyraldehyde, Form III (9)
12.3	3.28	3.10	12.3	100	40	40	100	2-Ethyl-butanal
12.1	3.26	7.2	13.2	100	100	90	6*	2-Butanone, Form II
12.4	3.25	3.36	12.4	100*	82	65	100*	<i>iso</i> -Butyraldehyde, Form I
13.4	3.22	3.64	13.4	100	50	30	100	<i>n</i> -Butyraldehyde, Form I
13.4	3.16	15.0	15.0	100b	40	27*	27*	2-Methyl-2-ethyl-butanal
11.9—11.0								
11.7	4.82	3.55	11.7	100	35	30	100	2,2-Dimethyl-butanal
11.5	4.77	3.67	11.5	100	37	35	100	4-Methyl-pentanal
11.7	3.93	5.90	11.7	100	50	30	100	<i>iso</i> -Butyraldehyde, Form II (10)
11.8	3.91	4.11	11.8	100	70	50	100	<i>iso</i> -Valeraldehyde, Form II (10)
11.3	3.71	7.5	11.3	90	100	50	90	2,6-Dimethyl-4-heptanone
11.6	3.64	4.62	11.6	80*	100	40	80*	Benzil
11.7	3.50	3.48	13.7	100	38	29	16	<i>n</i> -Butyraldehyde, Form II (9)
11.5	3.48	3.15	11.5	100	70	50	100	4,4-Dimethyl-2-pentanone
11.4	3.46	8.1	16.0	60*	100	90	6*	$\alpha$ -Methyl-cyclopentanone
11.0	3.37	7.3	12.2	28	100	32	13*	1-Phenyl-1-heptanone
11.0	3.30	4.75	11.0	100	80	30	100	<i>n</i> -Propionaldehyde, Form II (9, 10)
11.0	3.27	3.87	11.0	100*	90	50	100*	$\beta$ -Methyl-cyclopentanone
11.0	3.24	9.2	11.0	75*	100	38	75*	9,10-Phenanthraquinone
11.5	3.24	3.98	11.5	100	75	60	100	Cyclohexanone
11.1	3.23	5.80	11.1	100	58	32	100	Cyclopentanone (9)
11.5	3.17	6.3	11.5	90	100bb	75	90	Salicylaldehyde
10.9—10.0								
10.8	9.5	3.18	10.8	75	100	90	75	Acetone, Form II
10.4	3.87	4.25	14.7	35	100	35	9	<i>d</i> -Fructose dioxane solvate (22)
10.6	3.61	12.5	12.5	66	100	78	78	2-Pentanone (9)
10.4	3.45	3.07	10.4	100	95	90	100	Formaldehyde
10.5	3.31	6.2	10.5	82	100	78	82	Phenylacetone (9)
10.6	3.25	6.6	11.3	55	100	25	17	Crotonaldehyde
10.8	3.15	3.77	10.8	95	100	90	95	4,6,6-Trimethyl-3-heptene-2-one
9.9—9.5								
9.5	3.75	3.24	17.0	50	100	75	20*	2-Octanone, Form I
9.6	3.25	4.35	9.6	100*	100	16	100*	<i>n</i> -Propionaldehyde, Form I
9.5	3.18	10.8	10.8	100	90	75	75	Acetone, Form II
9.4—9.0								
9.1	12.3	7.0	12.3	50	100	65	100	3,3,4-Trimethyl-4-pentene-2-one
9.4	3.35	4.23	9.4	100	90d	45	100	1-Phenyl-1-tetradecanone
9.0	3.34	5.82		100	95	75		2-Methyl-1-butene-3-one (20)
9.1	3.34	5.18		55	100	55		3-Ethyl-3-butene-2-one (20)
9.1	3.29	3.74	13.5	100	100	75	10	Potassium- <i>aci</i> -5-nitro-1-naphthyl tetradecyl ketone
9.3	3.26	5.79	9.3	75*	100	90	75*	Acetone, Form I
9.2	3.24	11.0	11.0	38	100	75*	75*	9,10-Phenanthraquinone
9.4	3.23	3.17	10.4	100	100	90	2	Acetaldehyde, Form I
9.2	3.20	6.8	9.2	100	92	38	100	Acetaldehyde, Form II (9, 10, 12)
8.9—8.5								
8.5	13.9	3.68		100	100	100		3,3,4,4-Tetramethyl-2-pentanone (20)
8.5	6.5	7.8	8.5	100	30	25	100	2-Methyl-9-10-anthraquinone
8.9	4.46	3.37	16.0	90	100	70	30*	Benzophenone
8.9	3.46	5.89	13.0	20	100	90	6	<i>p</i> -Quinone
8.4—8.0								
8.0	5.05	3.55	14.0	100	50	50	30*	3,4,4-Trimethyl-2-pentanone
8.2	3.54	3.46	8.2	100	75	75	100	Potassium <i>aci</i> -5-nitro-1-naphthyl methyl ketone
8.1	3.46	11.4	16.0	90	100	60*	6*	$\alpha$ -Methyl-cyclopentanone
8.3	3.40	5.30	10.6	65	100	40	8	4-Methyl-2,6-heptadione
8.0	3.36	7.2	10.7	55	100	75	3	Benzalacetone



TABLE II. NUMERICAL INDEX OF STRONGEST LINES ARRANGED IN HANAWALT GROUPING, (Cont'd)  
 $d_1, d_2$ , and  $d_3$  are the three strongest lines;  $d_4$  is the largest  $d$  value<sup>a</sup>.

$d_1$	$d_2$	$d_3$	$d_4$	$I_1$	$I_2$	$I_3$	$I_4$	2,4-Dinitrophenylhydrazones of:
8.2	3.29	4.83	10.4	60	100	80	40*	3,4-Dimethyl-2-pentanone
7.9—7.5								
7.8	14.9	3.44	14.9	30	100	56	100	4-Heptanone (9)
7.6	13.7	3.48	13.7	78	100	42	100	4-Methyl-2-pentanone (9)
7.8	13.6	5.18	13.6	65	100*	90	100*	2-Methyl-3-hexanone
7.5	13.2	3.47	13.2	48	100	70	100	2-Heptanone (9)
7.75	12.80	3.47	12.8	72	100	56	100	2-Hexanone (9)
7.8	12.5	4.32	12.5	90	100	60	100	2-Butanone, Form I (10)
7.8	8.5	6.5	8.5	25	100	30	100	2-Methyl-9,10-Anthraquinone
7.7	4.25	3.39	10.3	80	100	70	65	1-Phenyl-1-hexadecanone
7.5	3.71	11.3	11.3	50	100	90	90	2,6-Dimethyl-4-heptanone
7.6	3.48	12.9		85	100	85		3-Ethyl-3-pentene-2-one, Form I (20)
7.6	3.45	5.47	13.9	55	100	53	40*	4,4,5-Trimethyl-5-hexene-3-one
7.8	3.40	6.8	17.0	75	100	70	10*	Furfurylidene acetone
7.8	3.37	5.12	13.4	75	100	90	55	Propiophenone
7.8	3.34	12.8	17.0	40	100	75	20*	2-Octanone, Form II
7.7	3.26	6.2	11.7	34	100	50	29	Furfuraldehyde, Form III (9)
7.4—7.0								
7.10	12.60	3.54	12.60	76	100	37	100	3-Pentanone (9, 10)
7.00	12.3	9.1	12.3	65	100	50	100	3,3,4-Trimethyl-4-pentene-2-one
7.00	12.1	3.60		85	100	90		3-Ethyl-3-pentene-2-one, Form II (20)
7.2	12.1	3.26	13.2	90	100	100	6*	2-Butanone, Form II
7.3	5.21	5.43	14.0	75	100	40	25	<i>d</i> -Camphor
7.3	3.48	5.75	11.3	50	100	40	28	Benzal-acetophenone
7.4	3.44	3.30	14.5	75d	100	100	25	Potassium- <i>aci</i> -5-nitro-1-naphthaldehyde
7.3	3.37	11.0	12.2	32	100	28	13*	1-phenyl-1-heptanone
7.2	3.36	8.0	10.7	75	100	55	3	Benzalacetone
7.2	3.36	3.25	13.5	95	100	80	25	Cinnamylaldehyde
7.4	3.34	6.7	9.8	47	100	52	15	Acetophenone
7.0	3.34	4.86	13.1	100	50	35	30*	2-Methyl-3-pentanone
7.2	3.30	12.3	12.3	90	100	90*	90*	3-Methyl-2-butanone
7.3	3.30	5.73	13.5	100	100	75	70*	3,3-Dimethyl-2-butanone
7.2	3.20	15.4		90	100	85		3,4-Dimethyl-4-hexene-2-one, Form I (20)
7.1	3.18	3.56	13.8	90b	100*	40	13*	3,4-Dimethyl-4-pentene-2-one
7.2	3.17	14.0	14.0	100	90b	75*	75*	<i>o</i> -homö-Salicylaldehyde
6.9—6.5								
6.90	13.7	3.40	13.7	78	100	62	100	2,4-Dimethyl-3-pentanone (9)
6.5	12.7	4.28	12.7	80	100	40	100	<i>iso</i> -Valeraldehyde, Form I (10)
6.8	9.2	3.20	9.20	38	100	92	100	Acetaldehyde, Form II (9, 10, 12)
6.5	8.5	7.8	8.5	30	100	25	100	2-Methyl-9,10-anthraquinone
6.6	3.52	6.9	10.6	55	100	25	8	Butyrophenone
6.9	3.52	6.6	10.6	25	100	55	8	Butyrophenone
6.8	3.40	7.8	17.0	70	100	75	10*	Furfurylidene acetone
6.9	3.39	4.25	7.2	90	100b	40	20	Vanillin
6.7	3.34	7.4	9.8	52	100	47	15	Acetophenone
6.8	3.27	14.8		70	100	65		3,4-Dimethyl-4-hexene-2-one, Form II (20)
6.6	3.25	10.6	11.3	25	100	55	17	Crotonaldehyde
6.4—6.0								
6.2	3.31	10.5	10.5	78	100	82	82	Phenylacetone (9)
6.1	3.31	3.21	13.0	90	100	90	25*	Benzaldehyde
6.1	3.30	5.35	12.3	60	100	42	32	<i>p</i> -Cl-Acetophenone (9)
6.2	3.26	7.7	11.7	50	100	34	29	Furfuraldehyde, Form III (9)
6.1	3.19	3.91		100	90	60		1-Acetylcyclohexene (20)
6.3	3.18	3.26	12.2	90	100	75	70*	<i>p</i> -Homo-salicylaldehyde
6.3	3.17	11.5	11.5	75	100bb	90	90	Salicylaldehyde
5.99—5.75								
5.90	11.7	3.93	11.7	30	100	50	100	<i>iso</i> -Butyraldehyde, Form II (10)
5.80	11.1	3.23	11.1	32	100	58	100	Cyclopentanone (9)
5.82	9.0	3.34		75	100	95		2-Methyl-1-butene-3-one (20)
5.75	3.48	7.3	11.3	40	100	50	28	Benzal-acetophenone
5.89	3.46	8.9	13.0	90	100	20	6	<i>p</i> -Quinone
5.79	3.26	9.3	9.3	90	100	75*	75*	Acetone, Form I
5.74—5.50								
5.73	7.3	3.30	13.5	75	100	100	70*	3,3-Dimethyl-2-butanone
5.68	3.24	5.36	11.7	30	100	19	3	Furfuraldehyde, Form II (9)
5.49—5.25								
5.43	5.21	7.3	14.0	40	100	75	25	<i>d</i> -Camphor
5.47	3.45	7.6	13.9	53	100	55	40*	4,4,5-Trimethyl-5-hexene-3-one
5.34	3.40	13.8	13.8	75	100	75*	75*	3-Cyclopentylidenecyclopentanone
5.30	3.40	8.3	10.6	40	100	65	8	4-Methyl-2,6-heptadione
5.25	3.37	4.41	12.0	75	100	60	13*	Difurfurylidene acetone
5.34	3.35	12.4	12.4	55	100	60*	60*	2,2-Dimethyl-propanol
5.35	3.30	6.1	12.3	42	100	60	32	<i>p</i> -Cl-Acetophenone (9)
5.36	3.24	5.68	11.7	19	100	30	3	Furfuraldehyde, Form II (9)
5.24—5.00								
5.18	13.6	7.8	13.6	90	100*	65	100*	2-Methyl-3-hexanone
5.11	12.0	4.82	12.0	82	100	55	100	2,3,3-Trimethyl-butanal
5.05	8.0	3.55	14.0	50	100	50	30*	3,4,4-Trimethyl-2-pentanone
5.21	7.3	5.43	14.0	100	75	40	25	<i>d</i> -Camphor
5.12	3.37	7.8	13.4	90	100	75	55	Propiophenone
5.18	3.34	9.1		55	100	55		3-Ethyl-3-butene-2-one (20)
5.09	3.33	4.49	10.2	40	100	40	25	3,3,4-Trimethyl-2-pentanone
4.99—4.90								
4.95	12.3	3.48		100	100	100		3,4-Dimethyl-3-pentene-2-one (20)



TABLE II. NUMERICAL INDEX OF STRONGEST LINES ARRANGED IN HANAWALT GROUPING, (Cont'd)  
 $d_1, d_2$ , and  $d_3$  are the three strongest lines;  $d_4$  is the largest  $d$  value<sup>a</sup>.

$d_1$	$d_2$	$d_3$	$d_4$	$I_1$	$I_2$	$I_3$	$I_4$	2,4-Dinitrophenylhydrazones of:
4.89—4.80								
4.82	12.0	5.11	12.0	55	100	82	100	2,3,3-Trimethyl-butanal
4.82	11.7	3.55	11.7	35	100	30	100	2,2-Dimethyl-butanal
4.86	7.0	3.34	13.1	35	100	50	30*	2-Methyl-3-pentanone
4.83	3.29	8.2	10.4	80	100	60	40*	3,4-Dimethyl-2-pentanone
4.79—4.70								
4.77	11.5	3.67	11.5	37	100	35	100	4-Methyl-pentanal
4.75	11.0	3.30	11.0	30	100	80	100	<i>n</i> -Propionaldehyde, Form II (9, 10)
4.77	3.99	3.69	25.4	s	s	s	s	<i>n</i> -Tridecanal (21)
4.75	3.96	3.71	22.4	s	s	s	s	<i>n</i> -Undecanal (21)
4.73	3.91	3.65	24.0	s	s	s	s	<i>n</i> -Dodecanal (21)
4.72	3.69	3.26	21.1	s	s	s	s	<i>n</i> -Decanal (21)
4.72	3.68	3.26	19.6	s	s	s	s	<i>n</i> -Nonanal (21)
4.69—4.60								
4.63	4.45	3.76	17.8	s	s	s	s	<i>n</i> -Heptanal (21)
4.62	3.64	11.6	11.6	40	100	80*	80*	Benzil
4.59—4.50								
4.58	4.22	3.74	19.2	s	s	s	s	<i>n</i> -Octanal (21)
4.49—4.40								
4.46	8.9	3.37	16.0	100	90	70	30*	Benzophenone
4.45	4.63	3.76	17.8	s	s	s	s	<i>n</i> -Heptanal (21)
4.48	3.53	3.28	14.3	100	75	55	8*	<i>dl</i> -Citral
4.41	3.37	5.25	12.0	60	100	75	13*	Difurfurylidene acetone
4.49	3.33	5.09	10.2	40	100	40	25	3,3,4-Trimethyl-2-pentanone
4.39—4.30								
4.33	12.6	3.28	12.6	26	100	83	100	<i>n</i> -Butyraldehyde, Form III (9)
4.35	9.6	3.25	9.6	16	100*	100	100*	<i>n</i> -Propionaldehyde, Form I
4.29—4.20								
4.28	12.7	6.5	12.7	40	100	80	100	<i>iso</i> -Valeraldehyde, Form I (10)
4.23	12.5	7.8	12.5	60	100	90	100	2-Butanone, Form I (10)
4.23	9.4	3.35	9.4	45	100	90d	100	1-Phenyl-1-tetradecanone
4.25	7.7	3.39	10.3	100	80	70	65	1-Phenyl-1-hexadecanone
4.22	4.58	3.74	19.2	s	s	s	s	<i>n</i> -Octanal (21)
4.25	3.87	10.4	14.7	35	100	35	9	<i>d</i> -Fructose dioxane solvate (22)
4.25	3.39	6.9	7.2	40	100b	90	20	Vanillin
4.20	3.17	3.20	13.7	58	100	76	40	Furfuraldehyde, Form I (9)
4.19—4.10								
4.11	11.8	3.91	11.8	50	100	70	100	<i>iso</i> -Valeraldehyde, Form II (10)
3.99—3.90								
3.91	11.8	4.11	11.8	70	100	50	100	<i>iso</i> -Valeraldehyde, Form II (10)
3.93	11.7	5.90	11.7	50	100	30	100	<i>iso</i> -Butyraldehyde, Form II (10)
3.98	11.5	3.24	11.5	60	100	75	100	Cyclohexanone
3.91	6.1	3.19		60	100	90		1-Acetylcyclohexene (20)
3.99	4.77	3.69	25.4	s	s	s	s	<i>n</i> -Tridecanal (21)
3.96	4.75	3.71	22.4	s	s	s	s	<i>n</i> -Undecanal (21)
3.91	4.73	3.65	24.0	s	s	s	s	<i>n</i> -Dodecanal (21)
3.96	3.16	3.24	14.2	50	100	75	20*	<i>m</i> -Nitrobenzaldehyde
3.89—3.80								
3.87	11.0	3.27	11.0	50	100*	90	100*	$\beta$ -Methyl-cyclopentanone
3.87	10.4	4.25	14.7	100	35	35	9	<i>d</i> -Fructose dioxane solvate (22)
3.83	3.24	14.0	14.0	65	100	80*	80*	Dibenzalacetone
3.79—3.70								
3.72	15.5	3.28	15.5	100	100	80	100	<i>n</i> -Hexanal
3.71	11.3	7.5	11.3	100	90	50	90	2,6-Dimethyl-4-heptanone
3.74	9.1	3.29	13.2	75	100	100	10	Potassium- <i>aci</i> -5-nitro-1-naphthyl tetradecyl ketone
3.71	4.75	3.96	22.4	s	s	s	s	<i>n</i> -Undecanal (21)
3.76	4.63	4.45	17.8	s	s	s	s	<i>n</i> -Heptanal (21)
3.74	4.58	4.22	19.2	s	s	s	s	<i>n</i> -Octanal (21)
3.78	3.66	3.25	15.1	s	s	s	s	<i>n</i> -Valeraldehyde (21)
3.75	3.24	9.5	17.0	100	75	50	20*	2-Octanone, Form I
3.77	3.15	10.8	10.8	90	100	95	95	4,6,6-Trimethyl-3-heptene-2-one
3.69—3.60								
3.68	13.9	8.5		100	100	100		3,3,4,4-Tetramethyl-2-pentanone (20)
3.64	13.4	3.22	13.4	30	100	50	100	<i>n</i> -Butyraldehyde, Form I
3.61	12.5	10.6	12.5	100	78	66	78	2-Pentanone (9)
3.60	12.1	7.0		90	100	85		3-Ethyl-3-pentene-2-one, Form II (20)
3.64	11.6	4.62	11.6	100	80*	40	80*	Benzil
3.67	11.5	4.77	11.5	35	100	37	100	4-Methyl-pentanal
3.69	4.77	3.99	25.4	s	s	s	s	<i>n</i> -Tridecanal (21)
3.65	4.73	3.91	24.0	s	s	s	s	<i>n</i> -Dodecanal (21)
3.69	4.72	3.26	21.1	s	s	s	s	<i>n</i> -Decanal (21)
3.68	4.72	3.26	19.6	s	s	s	s	<i>n</i> -Nonanal (21)
3.66	3.78	3.25	15.1	s	s	s	s	<i>n</i> -Valeraldehyde (21)
3.59—3.50								
3.54	12.60	7.10	12.60	37	100	76	100	3-Pentanone (9, 10)
3.55	11.7	4.82	11.7	30	100	35	100	2,2-Dimethyl-butanal
3.50	11.7	3.48	13.7	38	100	29	16	<i>n</i> -Butyraldehyde, Form II (9)
3.54	8.2	3.46	8.2	75	100	75	100	Potassium- <i>aci</i> -5-nitro-1-naphthyl methyl ketone
3.55	8.0	5.05	14.0	50	100	50	30*	3,4,4-Trimethyl-2-pentanone
3.52	6.6	6.9	10.6	100	55	25	8	Butyrophenone
3.53	4.48	3.28	14.3	75	100	55	8*	<i>dl</i> -Citral
3.56	3.18	7.1	13.8	40	100*	90b	13*	3,4-Dimethyl-4-pentene-2-one
3.49—3.45								
3.48	13.7	7.6	13.7	42	100	78	100	4-Methyl-2-pentanone (9)

TABLE II. NUMERICAL INDEX OF STRONGEST LINES ARRANGED IN HANAWALT GROUPING, (Cont'd)  
 $d_1, d_2$ , and  $d_3$  are the three strongest lines;  $d_4$  is the largest  $d$  value<sup>a</sup>.

$d_1$	$d_2$	$d_3$	$d_4$	$I_1$	$I_2$	$I_3$	$I_4$	2,4-Dinitrophenylhydrazones of:
3.47	13.2	7.5	13.2	70	100	48	100	2-Heptanone (9)
3.47	12.80	7.75	12.80	56	100	72	100	2-Hexanone (9)
3.48	12.9	7.6		100	85	85		3-Ethyl-3-pentene-2-one, Form I (20)
3.48	12.3	4.95		100	100	100		3,4-Dimethyl-3-pentene-2-one (20)
3.48	11.7	3.50	13.7	29	100	38	16	<i>n</i> -Butyraldehyde, Form II (9)
3.48	11.5	3.15	11.5	70	100	50	100	4,4-Dimethyl-2-pentanone
3.46	8.2	3.54	8.2	75	100	75	100	Potassium- <i>aci</i> -5-nitro-1-naphthyl methyl ketone
3.46	8.1	11.4	16.0	100	90	60*	6*	$\alpha$ -Methyl-cyclopentanone
3.45	7.6	5.47	13.9	100	55	53	40*	4,4,5-Trimethyl-5-hexene-3-one
3.48	7.3	5.75	11.3	100	50	40	28	Benzal-acetophenone
3.46	5.89	8.9	13.0	100	90	20	6	<i>p</i> -Quinone
3.44—3.40								
3.44	14.9	7.8	14.9	56	100	30	100	4-Heptanone (9)
3.40	13.8	5.34	13.8	100	75*	75	75*	3-Cyclopentylidene cyclopentanone
3.40	13.7	6.90	13.7	62	100	78	100	2,4-Dimethyl-3-pentanone (9)
3.40	8.3	5.30	10.6	100	65	40	8	4-Methyl-2,6-heptadione
3.40	7.8	6.8	17.0	100	75	70	10*	Furfurylidene acetone
3.44	3.30	7.4	14.5	100	100	75 d	25	Potassium- <i>aci</i> -5-nitro-1-naphthaldehyde
3.39—3.35								
3.35	12.4	5.34	12.4	100	60*	55	60*	2,2-Dimethyl-propanal
3.36	12.4	3.25	12.4	65	100*	82	100*	<i>iso</i> -Butyraldehyde, Form I
3.35	9.4	4.23	9.4	90 d	100	45	100	1-Phenyl-1-tetradecanone
3.37	7.3	11.0	12.2	100	32	28	13*	1-Phenyl-1-heptanone
3.36	7.2	8.0	10.7	100	75	55	3	Benzalacetone
3.36	7.2	3.25	13.5	100	95	80	25	Cinnamylaldehyde
3.39	6.9	4.25	7.2	100 b	90	40	20	Vanillin
3.37	5.25	4.41	12.0	100	75	60	13*	Difurfurylidene acetone
3.37	5.12	7.8	13.4	100	90	75	55	Propiophenone
3.37	4.46	8.9	16.0	70	100	90	30*	Benzophenone
3.39	4.25	7.7	10.3	70	100	80	65	1-Phenyl-1-hexadecanone
3.34—3.30								
3.34	12.8	7.8	17.0	100	75	40	20*	2-Octanone, Form II
3.30	12.3	7.2	12.3	100	90*	90	90*	3-Methyl-2-butanone
3.30	11.0	4.75	11.0	80	100	30	100	<i>n</i> -Propionaldehyde, Form II (9, 10)
3.31	10.5	6.2	10.5	100	82	78	82	Phenylacetone (9)
3.34	9.1	5.18		100	55	55		3-Ethyl-3-butene-2-one (20)
3.34	9.0	5.82		95	100	75		2-Methyl-1-butene-3-one (20)
3.30	7.3	5.73	13.5	100	100	75	70*	3,3-Dimethyl-2-butanone
3.34	7.0	4.86	13.1	50	100	35	30*	2-Methyl-3-pentanone
3.34	6.7	7.4	9.8	100	52	47	15	Acetophenone
3.30	6.1	5.35	12.3	100	60	42	32	<i>p</i> -Cl-Acetophenone (9)
3.31	6.1	3.21	13.0	100	90	90	25*	Benzaldehyde
3.33	5.09	4.49	10.2	100	40	40	25	3,3,4-Trimethyl-2-pentanone
3.30	3.44	7.4	14.5	100	100	75 d	25	Potassium- <i>aci</i> -5-nitro-1-naphthaldehyde
3.29—3.25								
3.28	15.5	3.72	15.5	80	100	100	100	<i>n</i> -Hexanal
3.28	12.6	4.33	12.6	83	100	26	100	<i>n</i> -Butyraldehyde, Form III (9)
3.25	12.4	3.36	12.4	82	100*	65	100*	<i>iso</i> -Butyraldehyde, Form I
3.28	12.3	3.10	12.3	40	100	40	100	2-Ethyl-butanal
3.26	12.1	7.2	13.2	100	100	90	6*	2-Butanone, Form II
3.27	11.0	3.87	11.0	90	100*	50	100*	$\beta$ -Methyl-cyclopentanone
3.25	10.6	6.6	11.3	100	55	25	17	Crotonaldehyde
3.25	9.6	4.35	9.6	100	100*	16	100*	<i>n</i> -Propionaldehyde, Form I
3.29	9.1	3.74	13.5	100	100	75	10	Potassium- <i>aci</i> -5-nitro-1-naphthyl tetradecyl ketone
3.27	6.8	14.8		100	70	65		3,4-Dimethyl-4-hexene-2-one, Form II (20)
3.26	6.2	7.7	11.7	100	50	34	29	Furfuraldehyde, Form III (9)
3.26	5.79	9.3	9.3	100	90	75*	75*	Acetone, Form I
3.29	4.83	8.2	10.4	100	80	60	40*	3,4-Dimethyl-2-pentanone
3.26	4.72	3.69	21.1	s	s	s	s	<i>n</i> -Decanal (21)
3.26	4.72	3.68	19.6	s	s	s	s	<i>n</i> -Nonanal (21)
3.28	4.48	3.53	14.3	55	100	75	8*	<i>dl</i> -Citral
3.25	3.78	3.66	15.1	s	s	s	s	<i>n</i> -Valeraldehyde (21)
3.25	3.36	7.2	13.5	80	100	95	25	Cinnamylaldehyde
3.26	3.18	6.3	12.2	75	100	90	70*	<i>p</i> -Homo-salicylaldehyde
3.24—3.20								
3.24	14.0	3.83	14.0	100	80*	65	80*	Dibenzalacetone
3.22	13.4	3.64	13.4	50	100	30	100	<i>n</i> -Butyraldehyde, Form I
3.24	11.5	3.98	11.5	75	100	60	100	Cyclohexanone
3.23	11.1	5.80	11.1	58	100	32	100	Cyclopentanone (9)
3.24	11.0	9.2	11.0	100	75*	38	75*	9,10-Phenanthraquinone
3.23	9.4	3.17	10.4	100	100	90	2	Acetaldehyde, Form I
3.20	9.2	6.8	9.2	92	100	38	100	Acetaldehyde, Form II (9, 10, 12)
3.20	7.2	15.4		100	90	85		3,4-Dimethyl-4-hexene-2-one, Form I (20)
3.24	5.68	5.36	11.7	100	30	19	3	Furfuraldehyde, Form II (9)
3.24	3.75	9.5	17.0	75	100	50	20	2-Octanone, Form I
3.21	3.31	6.1	13.0	90	100	90	25*	Benzaldehyde
3.20	3.17	4.20	13.7	76	100	58	40	Furfuraldehyde, Form I (9)
3.24	3.16	3.96	14.2	75	100	50	20*	<i>m</i> -Nitrobenzaldehyde
3.19—3.15								
3.16	13.4	15.0	15.0	40	100 b	27*	27*	2-Methyl-2-ethyl-butanal
3.17	11.5	6.3	11.5	100 b b	90	75	90	Salicylaldehyde
3.15	11.5	3.48	11.5	50	100	70	100	4,4-Dimethyl-2-pentanone
3.15	10.8	3.77	10.8	100	95	90	95	4,6,6-Trimethyl-3-heptene-2-one
3.18	9.5	10.8	10.8	90	100	75	75	Acetone, Form II



TABLE II. NUMERICAL INDEX OF STRONGEST LINES ARRANGED IN HANAWALT GROUPING, (Cont'd)  
 $d_1, d_2$ , and  $d_3$  are the three strongest lines;  $d_4$  is the largest  $d$  value<sup>a</sup>.

$d_1$	$d_2$	$d_3$	$d_4$	$I_1$	$I_2$	$I_3$	$I_4$	2,4-Dinitrophenylhydrazones of:
3.17	9.4	3.23	10.4	90	100	100	2	Acetaldehyde, Form I
3.17	7.2	14.0	14.0	90b	100	75*	75*	<i>o</i> -homo-Salicylaldehyde
3.18	7.1	3.56	13.8	100*	90b	40	13*	3,4-Dimethyl-4-pentene-2-one
3.18	6.3	3.26	12.2	100	90	75	70*	<i>p</i> -homo-Salicylaldehyde
3.19	6.1	3.91		90	100	60		1-Acetylcyclohexene (20)
3.16	3.24	3.96	14.2	100	75	50	20*	<i>m</i> -Nitrobenzaldehyde
3.17	3.20	4.20	13.7	100	76	58	40	Furfuraldehyde, Form I (9)
3.14—3.10								
3.10	12.3	3.28	12.3	40	100	40	100	2-Ethyl-butanol
3.09—3.05								
3.07	10.4	3.45	10.4	90	100	95	100	Formaldehyde

<sup>a</sup> Symbols used in the Table; \*-I/I, value doubtful, b-broad line, bb-very broad line, d-doublet, s-strong

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Submitted January 8, 1960, revision received February 9, 1961

## Emission Spectrographic Analysis of 65/35 and 50/50 Magnesium-Aluminum Alloys

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### Abstract

An emission spectrographic method has been developed that has been found suitable for the determination of iron, silicon, chromium, lead, titanium, zinc, and tin in a concentration range of 0.07-1.0%. The method consists of dissolving the sample in hydrochloric and sulfuric acids and converting it to the sulfate. One percent nickel is added as an internal standard and the sample is mixed with 2 parts of graphite. The procedure is found to have an average coefficient of variation of 5.1% for all determinations and has been found suitable as a rapid production control method for magnesium-aluminum alloys of 65/35 and 50/50 compositions.

### Introduction

Many types of metal powders are used in the formulation of pyrotechnic compositions. The performance of these finely divided metal powders is influenced by the purity of the pyrotechnic mixture. Two types of commonly used alloys are 65/35 magnesium-aluminum alloy and 50/50 magnesium-aluminum alloy. The following impurities have been found to be present in the two types of alloys; iron, silicon, chromium, titanium, lead, zinc, and tin.

Wet chemical analysis of these alloys involves the use of large samples and laborious separations with the dis-

advantage of not being able to be used as a production control procedure. A spectrographic method was considered a suitable technique for the analysis of these two alloys.

A literature search revealed a scarcity of published methods for the analysis of magnesium-aluminum alloys of these compositions. Consequently preliminary investigation was made of general spectrographic techniques to find a method which could be adapted for the requirements of a quality control method. These methods included the briquette, solution (1), and dry powder techniques (3-5). After preliminary investigation it was decided that the dry powder method using an ac arc excitation with internal standardization technique offered the best basis for an analytical method.

### Experimental

#### Materials:

Reagent grade aluminum sulfate and magnesium sulfate were used for the preparation of synthetic mixtures. Reagent grade nickel oxide and high purity graphite powder were used to prepare the 1% nickel-graphite mixture.

### Preparation of NiO-Graphite Mixture For Use As Internal Standard (Mixture A)

One half g of nickel (0.6363 g of nickel oxide) and 4.5 g of graphite are placed in an agate mortar and ground together intimately. One tenth g of this mixture is mixed with 0.9 g of pure graphite. This mixture is equivalent to 1% nickel in graphite.

### Preparation of Synthetic 65/35 Magnesium-Aluminum Samples (Mixture B)

A mixture of 31.85 g of magnesium sulfate and 21.98 g of aluminum sulfate is placed in an agate mortar and ground together intimately. This mixture is equivalent to 9.900 g of magnesium-aluminum 65/35 alloy. To this mixture, sufficient amounts of the oxides of iron, silicon, chromium, titanium, lead, zinc, and tin are added to give a series of standards containing 0.07-1.0% of each of the elements listed. Sufficient nickel oxide mixture is added to give a concentration of 1.0% nickel. These standards are mixed with two parts of graphite and are analyzed using the conditions under Table I.

### Preparation of Synthetic 50/50 Magnesium-Aluminum Samples (Mixture C)

A similar procedure is used to prepare Mixture C except that 31.40 g of aluminum sulfate and 24.50 g of magnesium sulfate are used.

### Preparation of Magnesium-Aluminum Samples for Spectrographic Analysis

One half g of sample is weighed into a Vycor beaker. Five mg of nickel is added and the sample is moistened with water and dissolved in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated sulfuric acid. The solution is evaporated to dryness and placed in a muffle furnace at 600°C for ½ hr. The sulfate is mixed with 2 parts of graphite and is analyzed using the basic operating conditions found in Table I.

TABLE I. SPECTROGRAPHIC OPERATING CONDITIONS

Electrodes	Lower, UCP 5780 Upper, UCP 100 U
Analytical gap, mm	2.5
Excitation	ac arc
Voltage, v	2400
Current, amp	4
Slit width, $\mu$	30
Exposure, sec	40
Emulsion	Eastman SA-1
Developer	Kodak D-19, 4 min

### Results

The emulsion calibration curves are obtained by a stepped sector method and are used in the conversion of relative transmittance values of the lines to intensity ratios. The analytical line pairs used are listed in Table II.

The analytical curves are prepared from synthetic standards. In each case a straight line is obtained when relative intensity is plotted against concentration. The best straight line is obtained by expanding the straight line relationship between variable y (intensity ratio) and variable x (concentration). The relationship can be expressed  $\log y = m \log X + b$ . (2). This equation establishes the best relationship between x and y and is the best straight line through all the points x and y for each line pair (Table II). The reliability of estimates from this line is measured through the use of the standard error of estimate. The standard error of estimate is, by definition, the standard deviation of points about a line and is calculated by the method of Geffner (2) and are listed under Table II.

### Discussion

Since the choice of magnesium and aluminum lines

for internal standardization is very meager, several other elements were considered for use as internal standards (iron, nickel, copper). A 1% nickel concentration was chosen for the following reasons:

a. Nickel was absent from all samples examined spectrographically.

b. Nickel has a good distribution of spectral lines suitable for internal standardization in the region of inspection.

TABLE II.  
EQUATIONS OF LINES OF REGRESSION.  
DETERMINATION OF IMPURITY ELEMENTS IN MAGNESIUM/ALUMINUM ALLOYS<sup>a</sup>

Element	Line	St. Errors of Estimate		Equations of Lines of Regression
		65/35 Composition	50/50 Composition	
Ni	3003.63	I	—	Internal standard
Fe	3020.64	I	±11.9	$\log y = 0.8122 X + 0.7864$
Si	2881.56	I	±11.0	$\log y = 0.0883 X + 1.6162$
Cr	2843.25	II	±11.8	$\log y = 0.8229 X + 0.3431$
Ti	3234.50	II	±10.8	$\log y = 0.8270 X + 0.8480$
Pb	2833.07	I	±10.2	$\log y = 1.0210 X + 0.0577$
Zn	3345.02	I	±10.4	$\log y = 0.7148 X + 0.5945$
Sn	3175.02	I	±10.8	$\log y = 0.9178 X + 0.4748$
Ni	3003.63	I	—	Internal standard
Fe	3020.64	I	±12.0	$\log y = 0.7112 X + 0.7536$
Si	2881.56	I	±11.8	$\log y = 0.8548 X + 0.6817$
Cr	2843.25	II	±10.6	$\log y = 0.7684 X + 0.4448$
Ti	3234.50	II	±11.8	$\log y = 0.8903 X + 0.9061$
Pb	2833.07	I	±11.7	$\log y = 0.9046 X + 0.2404$
Zn	3345.02	I	±11.2	$\log y = 0.9708 X + 0.1223$
Sn	3175.02	I	±10.2	$\log y = 0.9071 X + 0.5053$

<sup>a</sup> X, concentration, and y, intensity ratio

c. The ionization potential of nickel is close to that of a majority of the elements under inspection.

Table III lists the results obtained by the described spectrographic procedure on 6 representative lots of magnesium-aluminum alloys. A statistical analysis of the data obtained on these lots as well as the data on the synthetic samples indicates good precision and accuracy for the method.

A consideration for extending the range of the analytical curves has indicated that this procedure can be applied to the determination of the listed impurities at higher concentration ranges by proper dilution of the sample with appropriate matrix material.

TABLE III. DETERMINATION OF METALLIC IMPURITIES IN MAGNESIUM/ALUMINUM ALLOYS

Lot No.	Metallic Impurities, %						
	Fe	Si	Cr	Ti	Pb	Zn	Sn
I	0.25	0.18	0.15	<0.07	0.09	<0.10	<0.07
II	0.21	0.17	0.19	<0.07	0.07	<0.07	<0.07
III	0.31	0.09	0.19	<0.07	0.08	<0.07	<0.07
IV	0.27	0.15	0.17	<0.07	0.09	0.09	<0.07
V	0.40	0.20	0.21	<0.07	0.11	<0.07	<0.07
VI	0.41	0.19	0.25	<0.07	0.12	0.08	<0.07
Coeff. of Variation %	4.0	5.0	7.0	—	10.0	—	—

### Acknowledgement

The author wishes to express his appreciation to Mr. E. F. Reese for his aid in the preparation of this publication.

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Submitted January 20, 1960, revision received February 10, 1961



# Light Source, Excitation, and High Temperature Cell Assembly For Raman Spectroscopy

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## Abstract

A Toronto-style light source and the excitation circuit designed for use with a Hilger E612 recording Raman spectrometer in this laboratory are described. The electrical circuits and accessories are designed for automatic or manual start and with safety devices for protection in event of various component failures. For measurements on specimens at elevated temperatures, a simple cell assembly capable of use at temperatures up to  $575^{\circ}\text{C}$  with a gradient of not more than  $\pm 5^{\circ}\text{C}$  at the maximum temperature limit is described.

## Introduction

Whereas descriptions of various features of Raman sources and excitation circuits have appeared in the literature, the information is widely scattered and frequently lacks the detail essential in the construction of the various components. The Toronto-style light source and the excitation circuits and assemblies described in the present paper are based from a survey of the literature and knowledge available to date. A complete schematic wiring diagram and a parts list for all important commercially available components have been included as a useful practical feature. The Raman cell assembly for measurements on specimens at high temperatures was designed as part of a broader program of structural studies on molten salt systems in progress in this laboratory.

## Source and Excitation Assembly

### Source and Housing

The Pyrex glass mercury arc was made locally in accord with the specifications submitted after a study of the literature (1) and private discussions (2). The lamp incorporates the small water-cooling spiral internally concentric with the main spiral of the arc (1, 2), and this additional cooling together with forced air cooling from a blower makes possible the use of arc currents as high as 30 amp before the spiral is excessively heated. Kovar metal cap-glass seals were used in place of the tungsten electrodes to eliminate the metal-through-glass seals and since the larger metal surface furnished better contact with the electrical lead wires. The design of the lamp in three views is illustrated in Figure 1. The vertical capillary T-tubes on the "knee bends" of the main electrode leads act as scavenger traps for traces of gas that may evolve during operation. The knee bend in Figure 1 is exaggerated and in good design should not rise appreciably above the base of the electrode chamber. The lamp spiral and electrode chambers were baked under high vacuum at  $250^{\circ}\text{C}$  for a period of 3 days before filling. Mercury of the highest purity was finally distilled into the electrode

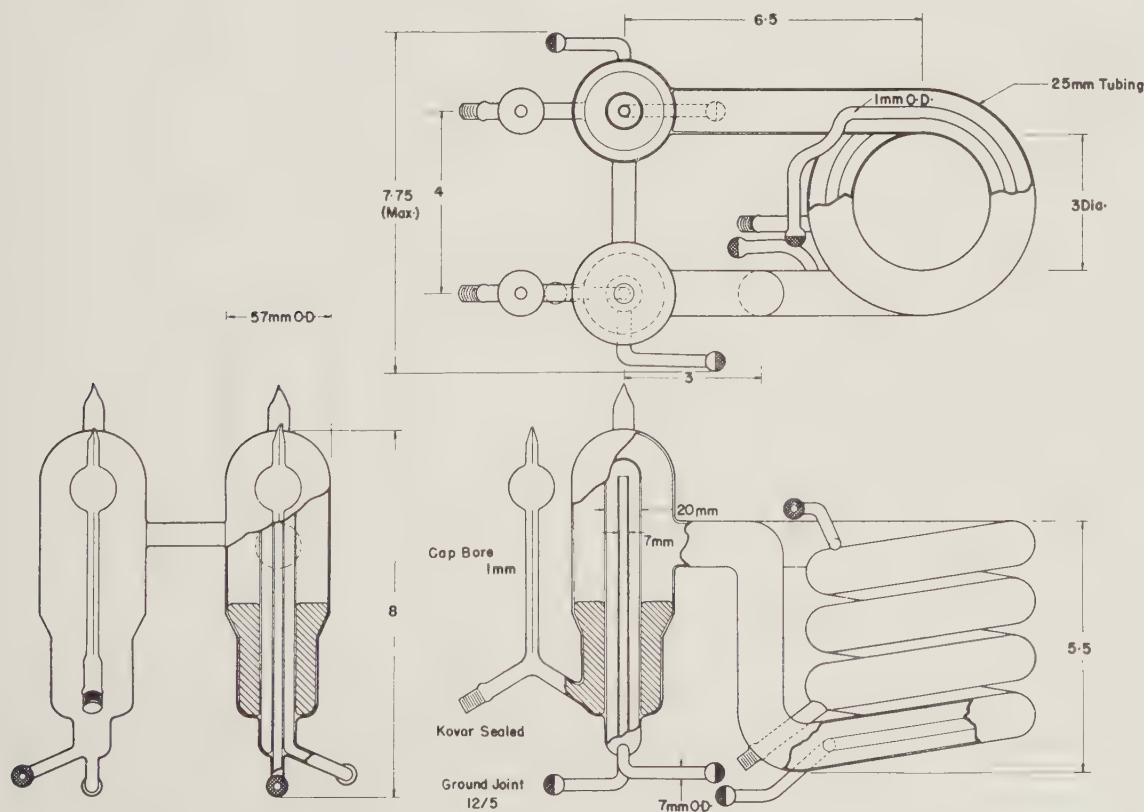


FIG. 1. MERCURY ARC LAMP

(Dimensions in inches unless otherwise noted)

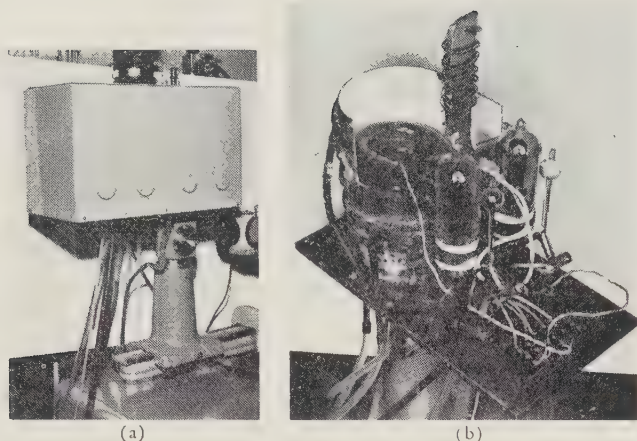


FIG. 2. PHOTOGRAPH OF LAMP HOUSING

(a) Assembled, (b) Cover removed to illustrate the positions of the various components.

chambers. No difficulty in striking the arc by the procedure to be described has been found with the above filling procedure rigidly observed.

The lamp housing is air-cooled by a blower on its top, exhausting through ports on the sides as illustrated in Figure 2. A resistance heater is installed in the air duct just above the lamp housing and a resistor in the blower circuit so that with these in operation a slow stream of heated air can be directed over the lamp as required initially during the heating period before striking the arc.

To reflect as much light as possible toward the sample a water-cooled metal shield was designed to surround the spiral of the mercury arc in position in the lamp housing (Figure 2). The shield was coated with magnesium oxide to reduce absorption and increase reflectivity. The surface is built up by first spraying a uniform coating on the brass using finely powdered oxide as an aqueous emulsion, and oven-baking at  $200^{\circ}\text{C}$  for approximately 8 hr. This coat is finally covered with very fine magnesium oxide by "smoking" the surface with burning magnesium ribbon held about 3 in. beneath the surface. The coating thus applied is firm and does not strip off unless touched.

The blue line of the mercury arc is isolated by Stamm's combination of liquid filters (3) in a cylindrical filter vessel with double chambers between the arc and the Raman sample tube. The innermost chamber contains rhodamine G (1 cm, 0.075 g/l) whereas aqueous  $\text{NaNO}_2$  at  $40^{\circ}\text{C}$  (1 cm, 88.5 g/100 ml) is circulated through the outermost chamber. In the center of the spiral and filter the straight Raman tube (9 ml sample) is guided into the correct position by a mounting base designed for this purpose.

### Excitation Circuits

The ac and dc circuits of the excitation assembly are illustrated in Figure 3 and the specifications in Table I. Protective circuits for the equipment in the event of overheating of the arc or its ancillaries, or failure of the water circulating devices, dc power, ac power, or the arc are included in this schematic as well as an automatic starting device in the driving circuit for the arc.

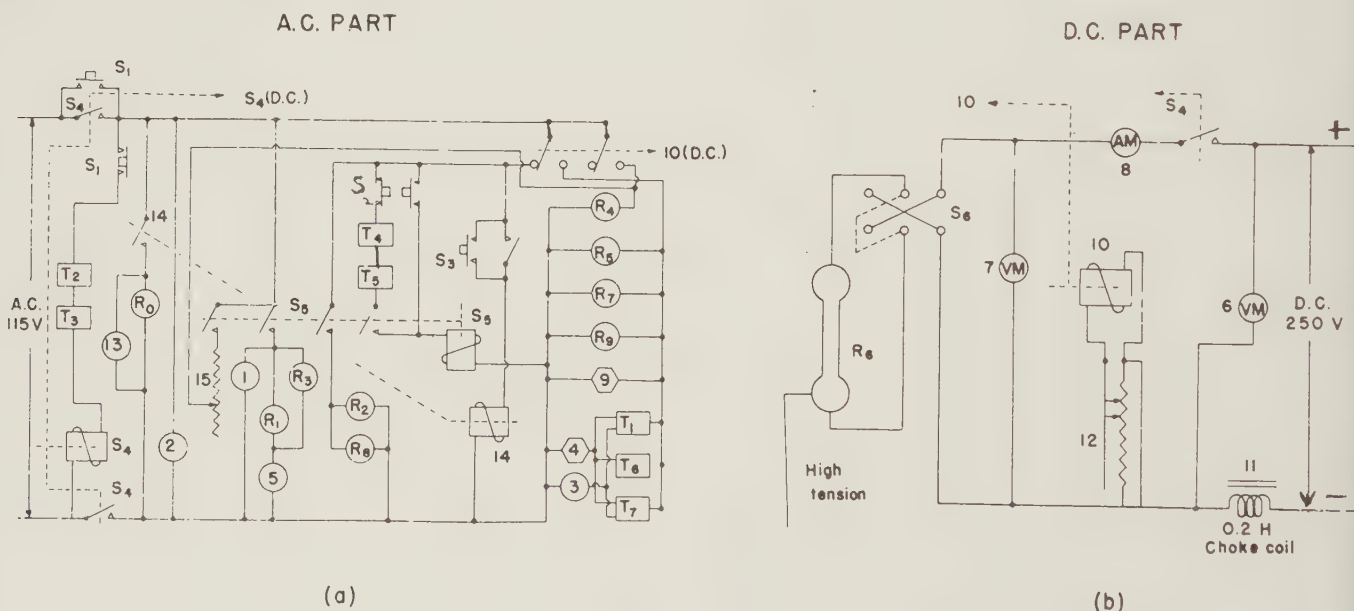


FIG. 3. RAMAN LIGHT SOURCE CIRCUIT DIAGRAM

- |                           |   |
|---------------------------|---|
| 1—Heater pilot light      | 12—Rheostat                                 |
| 2—Ready pilot light       | 13—High tension pilot light                 |
| 3—Mercury arc pilot light | 14—Relay                                    |
| 4—Buzzer                  | 15—Rheostat                                 |
| 5—Heater ammeter          | S <sub>1</sub> —Manual, for S <sub>1</sub>  |
| 6—D.c. main voltmeter     | S <sub>2</sub> —Manual, for S <sub>2</sub>  |
| 7—Mercury arc voltmeter   | S <sub>3</sub> —Pushbutton starter          |
| 8—Mercury arc ammeter     | S <sub>4</sub> —A.c. & d.c. mains, magnetic |
| 9—Clock                   | S <sub>5</sub> —Heater, magnetic            |
| 10—Relay                  | S <sub>6</sub> —Reversing                   |
| 11—Choke coil             |   |

### FROM RECEPTACLES ON CONTROL PANEL

- R<sub>1</sub>—Heater  
 R<sub>2</sub>—Hot water solenoid valve  
 R<sub>3</sub>—Heater (hot air)  
 R<sub>4</sub>—Blower  
 R<sub>5</sub>—Cold water solenoid valve  
 R<sub>6</sub>—Mercury arc  
 R<sub>7</sub>—Filter solution pump  
 R<sub>8</sub>—Hot water pump  
 R<sub>9</sub>—Cold water pump  
 R<sub>0</sub>—Neon transformer

### FROM SAFETY SWITCH TERMINALS ON CONTROL PANEL

- T<sub>1</sub>—Filter solution flowmeter  
 T<sub>2</sub>—Tap water pressure gauge  
 T<sub>3</sub>—Lamp house thermal switch  
 T<sub>4</sub>—Hot water flowmeter  
 T<sub>5</sub>—Hot air thermal switch  
 T<sub>6</sub>—Blower air sensing switch  
 T<sub>7</sub>—Cold water flowmeter



TABLE I. DESCRIPTION AND LIST OF COMPONENTS FOR SOURCE AND EXCITATION ASSEMBLY

Component Fig. Items	Description	Source"
1	Mercury arc	W.
2	Lamp Housing	R.P.I.
3	Microswitch	F.
T <sub>4</sub>	Thermoswitches, Miniature 32100-0, 2.5 amp, 115 v	F.
T <sub>3</sub> , T <sub>5</sub>		F.
1, 2, 3	Pilot lamps, 115 v, ac	T.
4	Buzzer and transformer, 6 v/115 v, ac	H.
5	Ammeter, ac, 0-50 amp	H.R.
6	Voltmeter, dc, 0-300 v	H.R.
7	Voltmeter, dc, 0-200 v	H.R.
8	Ammeter, dc, 0-80 amp	H.R.
9	Electric clock, 115 v, 60 cycle	H.R.
10	Guardian relay, Ser. 1R-505-G6, 6 v, dc, 10 amp, DPDT	H.R.
11	Choke coil, 0.2 h, 15 amp	G.E.
S <sub>1</sub> , S <sub>2</sub>	Pushbutton switches	R.P.I.
S <sub>3</sub>	Pushbutton SPDT Momentary switch	R.P.I.
S <sub>4</sub>	Magnetic switch No. 8, 45 amp, 115 v, TPST	R.P.I.
S <sub>5</sub>	Magnetic switch No. 12, 20 amp, 115 v, QPST	R.P.I.
S <sub>6</sub>	Reversing switch, DPDT, 40 amp	H.
4	5 Forsythe water-cooled rheostats, 15 amp/23 ohm, 28 amp/5 ohm	F.S.
6	Pyrex glass jar, O.D. 8 3/4 in., 10 in. high	W.
P <sub>2</sub> , P <sub>3</sub>	Constant Temp. Circulating Baths, Cat. No. 13-983	F.S.
P <sub>1</sub>	Braun Thermomix Const. Temp. Circulating Bath	W1.
S	Solenoid valves, S115, MOPD, 2000 psi, 60 cycle, ac	M.
F	Flowmeters, electrical contacts	W.
8	Water heater immersion unit, 2000 watt, Cat. No. F2-016	H.R.
9	Ashcroft pressure gauge with electrical contact, 0-100 psi, Cat. No. 1079	K.
	Air blower, Harco-Fasco, 115 v, 160 cfm	H.R.
	Neon Transformer, 15,000 v	N.
	6.5 kw, 240 v, dc motor generator set	G.E.
	Automatic voltage regulator (Diactor)	G.E.

"Sources: F., Fenwal, Inc., Ashland, Mass.; F.S., Fisher Scientific Co., New York 14, N. Y.; G.E., General Electric Co.; H., Hinsdill Electric Co., Troy, N. Y.; H.R., Herbach and Rademan, Inc., Philadelphia 7, Pa.; K., H. B. Kimmey Co., Inc., Albany, N. Y.; M., R. D. Marshall and Co., Inc., Albany, N. Y.; N., Troy Neon, Troy, N. Y.; R.P.I., Machine shop or stock, Rensselaer Polytechnic Inst.; T., Trojan Electronic Supply Co., Inc., Troy, N. Y.; W., Wilt Laboratory Glass Blowing, Inc., RR2 Watervliet N. Y.; and W1., Will Corporation, Rochester 3, N. Y.

For the dc source a 6.5 kw, 240 v motor generator set coupled with an automatic voltage regulator is used in this laboratory. This provides a power source within 0.5% regulation under reasonably steady state conditions, and the ripple superimposed on the dc voltage is approximately 1%. The use of a 5 kva voltage stabilizing transformer with a 5 kva selenium rectifier would serve as well but it is estimated that the voltage regulation would be 1% with a 5% ripple with this combination. A water-cooled rheostat and a 0.2 h choke coil\* are in series with the mercury arc lamp. The rheostat is set to deliver a dc current of 15 amp through the arc for normal measurements. Simultaneously 6 v are picked up from the rheostat to energize relay 10 when the arc is in operation. The choke coil specified above protects the dc source from the surge shock which occurs at the moment when the arc is struck. It was found in this laboratory that a flow-back of high tension voltage to the dc source occurred at the moment the arc struck unless rheostat 12 was connected to the negative side of the dc source. This was most probably because of some imperfections in the insulation of the rheostat being used.

To start the arc, manual switch S<sub>1</sub> is pressed, which activates the ac and dc mains through magnetic switch S<sub>4</sub>

\*The specification of this component in reference (1) as a 2-h unit is most probably a typographical error.

if the safety switches T<sub>2</sub> and T<sub>3</sub> are in the closed position. Prior to this operation the main tap water valve should have been opened. Safety switch T<sub>2</sub> protects the system in the event of a "no-water" operation (i.e., no tap water flow) through a pressure gauge with electric cutoff switch. The safety switch T<sub>3</sub>, which guards against further operation if the lamp housing should overheat, is in the closed position normally. When S<sub>4</sub> has closed, the "ready" pilot light, 2, is on. At this point switch S<sub>2</sub> is closed, activating the heating circuit through the magnetic switch S<sub>5</sub>. The "heater" pilot light, 1, turns on, the heater ammeter indicates the current through auxiliary heating coil in the hot water thermostat, and the hot water circulation through the lamp begins. Safety switch T<sub>4</sub> opens the circuit in the event of hot water flow failure whereas the thermoswitch T<sub>5</sub> serves to cut off the heating circuit in the event of the hot air flow failure. This heating operation takes from 20-30 min from the time S<sub>1</sub> was closed to start the arc. During the heating period the hot air from the blower fan aids in warming the walls of the lamp. When the hot water thermostat temperature reaches 95°C, the switch, 14, of the neon transformer, R<sub>0</sub>, automatically closes to deliver momentarily a high tension voltage (15,000 v) at the third electrode of the lamp, and activates a "high tension" pilot light, 13, simultaneously. The arc usually strikes with the first shock of high tension.

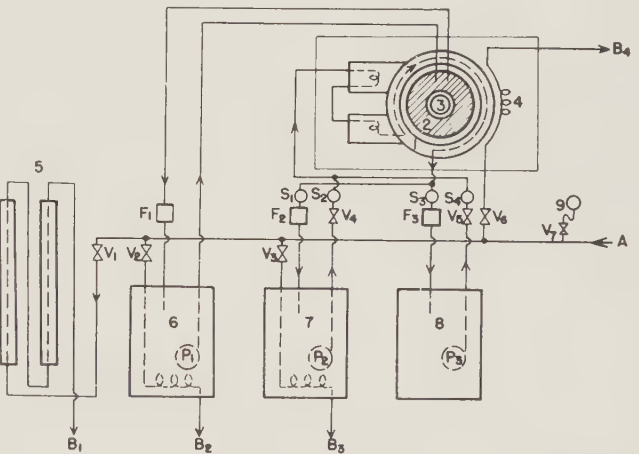


FIG. 4. RAMAN SOURCE FLOW-CIRCULATION SYSTEM

- 1—Mercury arc lamp

2—Filter solution

3—Sample tube

4—Water-cooled reflector

5—Water-cooled rheostats

6—Filter solution thermostat

7—Cold water thermostat

8—Hot water thermostat

9—Pressure gauge with electric cutoff switch

A—Tap water

B<sub>1</sub>—Drain from rheostat

B<sub>2</sub>—Drain from filter solution thermostat

B<sub>3</sub>—Drain from cold water thermostat

B<sub>4</sub>—Drain from reflector
- PUMPS—P

P<sub>1</sub>—For filter solution

P<sub>2</sub>—For cold water

P<sub>3</sub>—For hot water
- SOLENOID VALVES—S

Solenoid valves—S

S<sub>1</sub>—At input of cold water

S<sub>2</sub>—At output of cold water

S<sub>3</sub>—At input of hot water

S<sub>4</sub>—At output of hot water
- FLOWMETERS WITH ELECTRIC CONTACTS—F

F<sub>1</sub>—Filter solution

F<sub>2</sub>—Cold water

F<sub>3</sub>—Hot water
- VALVES—V

V<sub>1</sub>—For tap water to rheostat

V<sub>2</sub>—For tap water to filter soln. thermostat

V<sub>3</sub>—For tap water to cold water thermostat

V<sub>4</sub>—For cold water

V<sub>5</sub>—For hot water

V<sub>6</sub>—For tap water to lamp housing

V<sub>7</sub>—For pressure gauge

As the arc strikes, relay 10 is energized by the potential picked up from rheostat 12, and the cold air and cold water circuits are activated so that the cold air is forced into the lamp housing and cold water circulates through the lamp. A clock, which monitors the running time and pilot light, is also activated on the panel. In the event that there is a failure in any of the circulating systems, or the air blower, the alarm buzzer is activated.

A schematic arrangement of the components in the flow circulation system is illustrated in Figure 4. The thermostats 6, 7, and 8 are capable of circulating  $\text{NaNO}_2$  filter solution ( $40^\circ\text{C}$ ), cold water, and hot ( $95^\circ\text{C}$ ) water, respectively, through the appropriate part of the mercury arc lamp and filter vessel. The flowmeters,  $F_1$ ,  $F_2$ ,  $F_3$ , are the conventional pilot U-tube indicator style, each modified with three platinum-through-glass seals to make electrical contact with the mercury column in the U-tube. The flowmeters thus serve as safety switches to protect the equipment in the event of flow failure in any one of the three systems. Distilled water is used in thermostats 7 and 8. In the latter an additional heater is used so that the water can be raised to  $95^\circ\text{C}$  within 30 min from the time the starting switch  $S_1$  is pressed. When the temperature of the hot water is high enough, the switch of the neon transformer is activated to start the arc automatically. As the arc starts, relay 10 is activated, cutting off the whole heating circuit. The cold water circulation in place of the hot water is also automatically activated by the solenoid valves.

Since the  $\text{NaNO}_2$  solution becomes heated by radiation from the arc, the solution must be cooled. Rather than an additional jacket of cold circulating water between the arc and filter solution, in the present arrangement circulation of the  $\text{NaNO}_2$  solution kept at  $40^\circ\text{C}$  was adopted, with the advantage of avoiding the reduction of needless light absorption by the water layer in the alternate arrangement. The components of this thermostat-circulation system, including the pump, should be all glass, plastic, or stainless steel to minimize corrosion effects by the nitrite filter solution.

The rheostats, 5, filter and cold water thermostats, 6 and 7, and the reflection shield for the arc spiral, 4, are cooled by tap water. The pressure gauge-electrical switch, 9, guards the assembly in the event of no flow or a decrease in the rate of flow to a hazardously low level in this system. The valves  $V_1$ - $V_6$  enable flow rate adjustments as necessary in each circulating system and once set, should require no further attention. Only the valve  $V_7$  to the water main needs to be opened before the switch  $S_1$  is depressed for automatic starting of the arc.

A complete schematic wiring diagram for the control panel is illustrated in Figure 5, and a list of components is given in Table I.

### Discussion

Whereas the above arc and exciting circuit were designed for use with a Hilger E612 Recording Raman Spectrometer available in this laboratory, the unit is complete within itself and should serve equally well with any Raman spectrograph. An indication of the intensity of the source may be gained from the following examples. Using a slit width of 0.1 mm, a camera with  $f$  5.7 aperture, and Kodak 103a-O plates, the exposure times necessary for the Raman spectra of molten sodium nitrate, pure carbon tetrachloride, and an aqueous 2 M  $\text{AgNO}_3$  solution were 40 sec, 2 min, and 10 min, respectively. An exciting current of 15 amp was used through the arc in each case above.

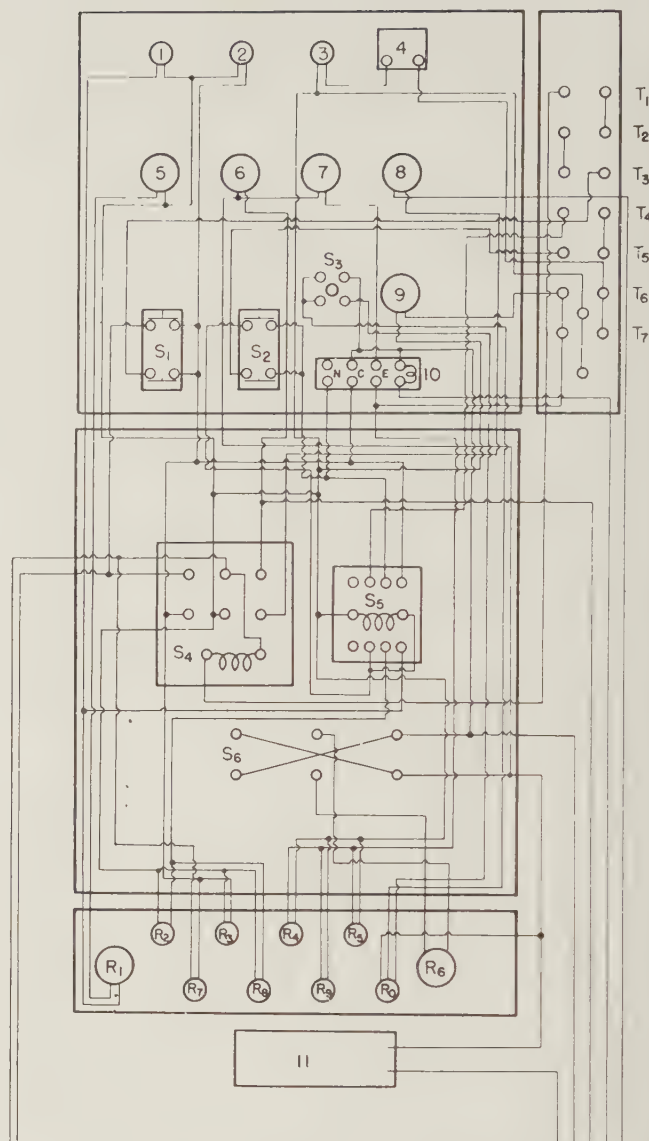


FIG. 5. WIRING DIAGRAM FOR CONTROL PANEL

- |                           |  |
|---------------------------|--|
| 1—Heater pilot light      | 2—Ready pilot light                            |
| 3—Mercury arc pilot light | 4—Buzzer                                       |
| 5—Heater ammeter          | 6—d.c. mains voltmeter                         |
| 7—Mercury arc voltmeter   | 8—Mercury arc voltmeter                        |
| 9—Clock                   | 10—Relay (N, normal; C, common; E, energizing) |
| 11—Choke coil             | 12—Rheostat                                    |

### RECEPTACLES—R

- |                                  |                                 |
|----------------------------------|---------------------------------|
| $R_1$ —Heater                    | $R_2$ —Hot water solenoid valve |
| $R_3$ —Spectrometer              | $R_4$ —Blower                   |
| $R_5$ —Cold water solenoid valve | $R_6$ —Mercury arc              |
| $R_7$ —Filter solution pump      | $R_8$ —Hot water pump           |
| $R_9$ —Cold water pump           | $R_0$ —Mercury arc starter      |

### SWITCHES—S

- |                           |                                      |
|---------------------------|--------------------------------------|
| $S_1$ —Manual, for $S_4$  | $S_2$ —Manual, for $S_3$             |
| $S_3$ —Pushbutton starter | $S_4$ —A.c. and d.c. mains, magnetic |
| $S_5$ —Heater, magnetic   | $S_6$ —Reversing                     |

### SAFETY SWITCH TERMINALS—T

- |                                  |                                       |
|----------------------------------|---------------------------------------|
| $T_1$ —Filter solution flowmeter | $T_2$ —Tap water pressure gauge       |
| $T_3$ —Lamp house thermal switch | $T_4$ —Hot water flowmeter            |
| $T_5$ —Hot water thermal switch  | $T_6$ —Blower air flow sensing switch |
| $T_7$ —Cold water flowmeter      |                                       |



In the present laboratory, as previously stated, the arc usually strikes on application of the first high tension discharge from the Neon sign transformer. Even if the arc fails to light immediately after the first "kick" of the high tension, it starts within a few minutes after this discharge. A provision for a "manual" start has been incorporated in the circuit. Depression of  $S_3$  at any time activates the neon transformer discharge.

### High Temperature Cell Assembly

The complete unit is illustrated in Figure 6, and consists of a heating assembly and a Raman cell of modified design to be used in the working space, 3 in. diam. by 10 in. long, defined by the Toronto arc.

### Heating Assembly

The principle of design is to have a coil of fine resistance wire on the Raman tube as the primary source of heat. Natural convection would cause the heat to rise and the lower part of the tube would remain cool. A current of preheated air passing from top to bottom is used to force the heat downwards, having its flow rate and temperature controlled to give the most uniform temperature over the length of the tube.

The Raman tube A (10 mm o.d.) is wound with resistance wire (Kanthal, B and S No. 24) platinized to reduce reflectance, and held, at its upper end, in a silica tube B of 20 mm o.d. by a steel wire clip. The two tubes are positioned at the base by a tapered cylindrical brass sleeve C with a removable glass window D. The latter prevents hot air escaping over the surface of the reflecting prism. The top of the silica tube is fitted with a gas inlet tube E, a thermocouple well F, and an opening for the lead to the resistance windings G. A side arm tube from the base of the silica tube is the gas outlet and the exit for one of the electric leads. The part of the silica tube extending above the mercury arc and gas inlet tube is insulated with a 1/4-in. layer of asbestos.

Surrounding the two tubes but separated from them by an air gap is a two-compartment Pyrex jacket I; the inner compartment is evacuated and the outer compartment is a filter jacket through which the conventional filter solution kept at any desired temperature is circulated. If depolarization data are required, two Polaroid cylinders with axes at right angles may be alternately slipped over the outside of the filter jacket (3).

Connected to the gas inlet E via a ground glass joint is a coil of 6 mm o.d. silica tubing, J, of total length 150 cm, situated in a furnace as shown in Figure 1. This is to preheat the air stream which is admitted at monitored flow rates over the Raman cell in the assembly.

### High Temperature Raman Cell

The design of the Raman tube in the region of the optically flat window was found quite critical for high temperature work. A design found satisfactory in this laboratory is shown in the insert of Figure 6. The important point is that the curvature of the tube wall above the window is slightly convex inwards. Some details on the adjustable brass base plate are also shown in the insert.

The inorganic compounds being investigated in this laboratory in the liquid state are all relatively high-melting (m.p. 300°C and higher). A filling technique after the method described elsewhere in detail by Boston and Smith (4) is used in this laboratory. The sample is placed in an ampoule and is separated from the Raman tube below by

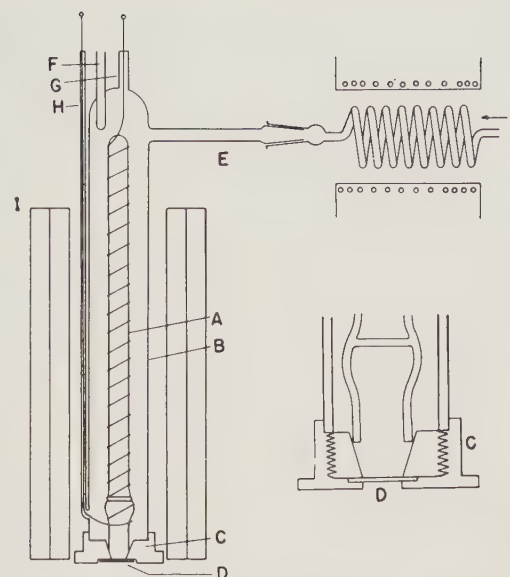


FIG. 6. ARRANGEMENT OF RAMAN CELL ASSEMBLY AND AUXILIARY EQUIPMENT FOR HIGH TEMPERATURE INVESTIGATIONS

- |                                      |                                       |
|--------------------------------------|---------------------------------------|
| A—Raman tube                         | B—Silica tube                         |
| C—Brass sleeve                       | D—Glass window                        |
| E—Inlet from preheater               | F—Thermocouple well                   |
| G—Resistance winding                 | H—Gas outlet and resistance wire exit |
| I—Two-compartment Pyrex glass jacket | J—Silica coil gas preheater           |

a fritted glass disc. When the sample has been vacuum dried and melted (with a small auxiliary furnace), a slight positive pressure of dry nitrogen gas admitted above the sample forces the molten salt with simultaneous filtration through the fritted glass disc into the Raman tube. The Raman tube may be hermetically sealed under vacuum with a glass torch to remove it from the system. Before the transfer of the Raman cell from the filling apparatus to the lamp housing, the molten salt solidifies and cools. The modified design of the Raman tube described above has been most effective in withstanding the strain thus imposed on the glass in the region of the cell window. When the sample has cooled, the tube is wound with the resistance wire, and the top and bottom of the cell walls are blackened in the conventional manner with an inorganic pigment.

### Discussion

$\text{NaNO}_3$  (m.p. 308°C) and  $\text{HgCl}_2$  (m.p. 280°C) are illustrative of two inorganic compounds investigated successfully with this technique. With molten sodium nitrate, the Raman measurements were extended to 450°C with no indication of bubble formation or decomposition of the sample. Exposure times, using Kodak 103a-0 plates were 2 and 5 min without and with Polaroid filters respectively. Exposures up to 20 min were made without excessive background.

$\text{HgCl}_2$  is an example of an inorganic salt with a very limited temperature range for the liquid state (m.p. 280°C, b.p. 302°C). For such compounds the thermal gradients must be small and local hot spots must be virtually nonexistent in the Raman cell assembly. At 300°C, a temperature gradient of  $\pm 2^\circ\text{C}$  is readily achieved in the present assembly. It was noted that vapor bubbles would form along the line of the Kanthal resistance windings if

the applied voltage was slightly too high. The light scattered from these bubbles made Raman measurements nearly impossible. With more careful voltage control this vapor formation was readily avoided. For mercuric chloride, sharp spectra were photographed with as little as 10 sec exposure time. For depolarization measurements, the time increased to approximately 30 sec.

For inorganic salts which can be contained in the molten state in Pyrex or silica Raman cells, the present assembly is readily adapted to most instruments with the Toronto-type arc for the investigation of samples up to 550 and 1600°C respectively. For use at temperatures greater than 500° (e.g., 1000°), an important modification would be to decrease still more the spacing between the Raman tube and the inside wall of the silica furnace tube (Figure 1, A-B). Increasing the wattage of the resistance windings on the Raman cell is not sufficient for this purpose since the gas flow is important to minimize the temperature gradients in the assembly. In the present work it was observed that if the spacing between the units was 7.5 mm, the maximum temperature obtained was 320°C, with a gradient of  $\pm 20^\circ\text{C}$ ; with the clearance reduced to 5 mm between the walls, the maximum temperature obtained was 575°C, with a gradient of  $\pm 5^\circ\text{C}$ . With the latter at 300°C, the temperature gradient could be decreased to  $\pm 2^\circ\text{C}$ . This rate of gas flow, which seems a critical factor, must be arbitrarily adjusted to obtain the optimum performance of the assembly at each temperature.

Where the melts are too reactive, a radically different design for the Raman cell assembly in which the surface of the molten material itself is the optical window, and

the melt is contained in a platinum or refractory beaker is necessary. This approach has been recently developed successfully by Bues and has been described in recent publications (5).

### Acknowledgments

This work was made possible in part by support received from the National Science Foundation, Washington, D.C., and a grant-in-aid from the Trustees' Research Fund, Rensselaer Polytechnic Institute. A sample of inorganic pigment (No. F-2302) from Ferro Corporation, Cleveland, is gratefully acknowledged. The authors wish to thank Dr. R. F. Stamm, American Cyanamid Company, for most helpful discussions on various phases of the design problem and Professor T. F. Young, University of Chicago, for information on the application of the MgO coating. The assistance of L. F. Friedman in the construction of the lamp housing is acknowledged.

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Submitted January 27, 1960

## Notes

### Gas Identification with Microwave Excitation and a Small Spectroscope-Camera

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The combination of a microwave excitation source with a small spectroscope mounted in focus to a 35 mm camera (Figure 1) has proved to be rapid and relatively simple for the identification of various gases. The source is a standard magnetron unit, type CMD-4, from Raytheon which produces microwave power of 10 to 100 watts at a frequency of 2450 megacycles. Both the excitation source and the spectroscope-camera are compact and portable and can be used under a wide variety of conditions. All parts are comparatively inexpensive and easily assembled.

The spectroscope used is a small glass prism instrument manufactured by Carl Zeiss. It covers the visible region, 390—760  $m\mu$ , with about 15 mm total dispersion. Although the dispersion is not great, this is partially compensated for by the good resolving power of the spectroscope, approximately 2 Å in the region of 4300 Å. Since each spectrogram occupies but one frame of the 35 mm film, a number of exposures are made without reloading the camera. For the approximate location of spectral lines or bandheads, a scale is superimposed over the spectrogram. For greater precision the scale is calibrated with known simple spectra, such as those of mercury and sodium.

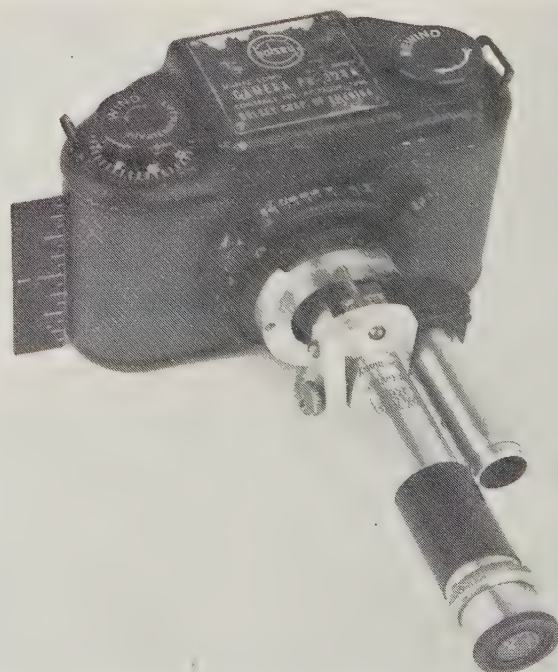


FIG. 1. COMBINATION SPECTROSCOPE-CAMERA FOR IDENTIFICATION OF GASES BY THEIR EMITTED SPECTRA



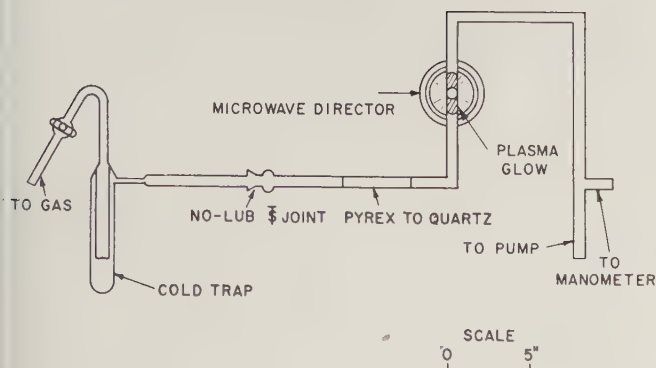


FIG. 2. DESIGN OF APPARATUS FOR PRODUCING SPECTRA OF GASES BY MICROWAVE EXCITATION

Unknown gases are identified by the comparison of their spectrograms with reference spectrograms, either directly or on a comparator-densitometer so designed for film. The reference spectrograms can be made from standard lamps or from the spectra produced in an apparatus designed originally for discharge and afterglow studies (Figure 2). This design is a modification of the one by Beale and Broida (1). Known gases at reduced pressures are excited by the microwave source directed at one point in the line of the discharge apparatus. The plasma glow is triggered with a Tesla coil discharge. Since it is practical to obtain only a limited number of reference spectrograms of molecular spectra, it is often necessary for the identification of band systems to locate the bandheads as closely as possible and then to refer to published tables of molecular spectra such as those found in Pearse and Gaydon (2). Reference spectrograms taken with the spectroscope-camera are shown in Figure 3.

Gases for identification originate from several sources. One is the gas in an electronic tube; another is a gas or gases evolved from a reaction of some kind and sealed in an electrodeless discharge tube. A method for making electrodeless discharge tubes is described by Meggers and Westfall (3). For high efficiency of excitation, the tubes are coupled to the microwave source either as a section of the inner conductor of a tuneable length of coaxial line (4) or inside a tuneable resonance cavity (5, 6). However, for most conditions which involve only the identification of a gas, the microwave directors supplied by the manufacturer are sufficient. With these directors a large variety of shapes of sealed tubes can be excited. In several cases solid materials were placed in the line of the discharge apparatus (Figure 2), and the gases were excited as they evolved from the solid. The slit of the spectroscope is brought as close as practical to the plasma glow. The timing mechanism of the camera is used to obtain correct exposures which vary from a fraction of a sec to several hrs depending on the intensity of the plasma glow and the speed of the film used.

The spectroscope-camera described has also proved to be useful for the study of the luminescent spectra of several materials (7-9). Similar, but faster and more complex, combinations of a 35 mm camera with a prism (10) and with a grating (11) to make high-speed spectrographs are discussed in the literature.

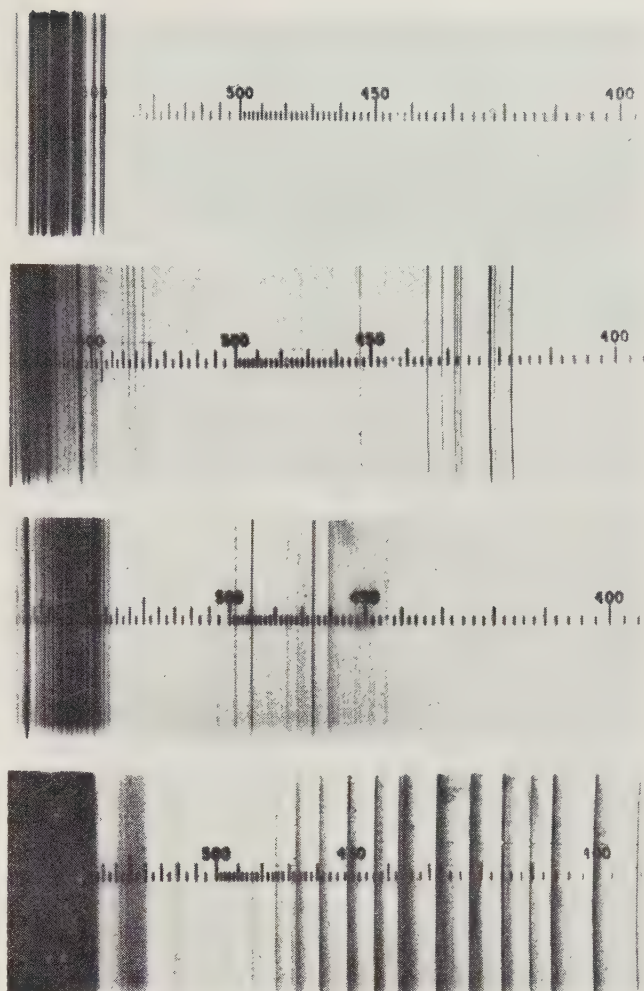


FIG. 3. REFERENCE SPECTROGRAMS (TOP TO BOTTOM) NEON, ARGON, HYDROGEN, AND NITROGEN

Overexposed in 600-700  $m\mu$  region to emphasize the narrow bands in 400-500  $m\mu$  region.

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Submitted July 1, 1960

## Cement Coated Wheel Technique for Spectrographic Analyses

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The spectrographic analysis of alloys is frequently complicated in industrial laboratories where samples may be presented as large plates and blocks, chips from weld spots, turnings, or filings. The variety of sample sizes and shapes makes it difficult to establish standard sampling practice and excitation conditions.

In the analysis of aluminum alloys, the heat of the dc arc forms refractory aluminum oxide and results in erratic spectra. Although spark excitation is relatively free of this objection, its spectra may lack precision for other reasons; for example, fine powders tend to blow away, chips melt at the edges as the spark tends to concentrate there, while plates and blocks remain at a relatively uniform temperature as desired for spark excitation.

The problems were solved by reducing all samples to homogeneous filings which were then glued to a graphite wheel electrode and subsequently sparked. Spectra obtained by this method are reproducible, and precision and accuracy of the analyses are satisfactory even though the samples may have widely differing metallurgical histories.

Blank analyses using a non-ferrous alloy, Rene 41†, hardness of Rockwell C45, demonstrated that contamination in the use of the files was negligible (Nominal Composition: Cr 19%; Co 11%; Mo 9%; Ti 3%; Al 1.5%; remainder Ni).

The idea of glueing the sample to the electrode was suggested by Danielsson *et al* (1) who used a moving adhesive tape to hold the sample and feed it into the spark gap; this, however, seemed to present too many technological difficulties, and the more simple cement-coated wheel techniques was developed.

The samples are reduced to small particle size (100 mesh) by clamping them in a vise and filing the samples with a fine mill file. About 150 mg of filings are caught on a sheet of paper. Turnings are first pressed by means of the pellet press to 1/4 or 1/2 in. diam. pellets, and these can then be filed as any larger form of sample. The smallest

TABLE I.

### APPARATUS AND SPECTROGRAPHIC CONDITIONS

*Spectrograph.* 1.5 meter ARL grating spectrograph with 7A/mm. dispersion.  
*Excitation source.* ARL Multisource unit, Model 22  
*Film.* Kodak SA No. 1, 35 mm film  
*Densitometer.* ARL Projection Comparator  
*Electrodes.* National preformed spectrographic graphite electrodes Cat. No. L-4075 as the sample electrode and Cat. No. L-3957 as counter electrode  
*Sample electrode system.* The sample electrode system consists of the rotating electrode frequently used for the analysis of liquid samples. In this specific case the graphite wheel is held by friction on a tapered, tungsten shaft which is turned by a synchronous motor at the rate of 10 rpm.  
*Rubber cement or glue.* Carter's Clean Grip rubber cement  
*Pellet press.* ARL No. 3501 Briquetting machine

### SOURCE AND EXPOSURE CONDITIONS

Charging phase	180°	Resistance, ohm	100
Discharge point	90°	Slit width, $\mu$	30
Capacitance, $\mu$ f	4	Exposure time, sec	15
Inductance, $\mu$ h	480		

†Available from General Electric Corp., Detroit, Mich.

possible particle size is advantageous, since the particle is then volatilized entirely by the spark, thus avoiding distillation and oxidation effects.

The graphite wheel that is to become the sample electrode is held temporarily on a tapered graphite rod. The rubber cement is applied by rotating the wheel slowly against the applicator brush so that an even layer of cement is deposited on the wheel's circumference. The sample filings are spread on a paper in a thin layer and the wheel is rolled over these filings so that the cement-coated surface will pick up the filings in a smooth, even layer. The cement is allowed to dry a few min after which the prepared wheel is transferred to the rotating shaft in the excitation chamber of the spectrograph.

TABLE II. ANALYSIS AND INTERNAL STANDARD LINES

Element	Line, Å
Mg	2781.3
Mn	2610.2
Si	2514.3
Cr	2677.2
Cu	2961.2
Al <sup>a</sup>	2669.2

<sup>a</sup> Internal Standard line

Apparatus, source, and exposure conditions are shown Table I with the lines for analysis and internal standard given in Table II.

Calibration was originally made using filings from Spex Industries' wrought aluminum alloy swatches (4" x 1" pieces of aluminum alloy)\*. The analysis sheet supplied with the swatches listed only nominal composition; however, the Aluminum Company of America Handbook (2) listed the chemical composition limits. These ranges were plotted on semi-log graph paper versus intensity ratio of the element to the aluminum 2669 standard line. Using the nominal composition of these swatches as a guide, a straight line could be drawn through all percentage ranges quite close to the listed chemical compositions.

An example of the precision and accuracy obtainable is shown in the analysis of an aluminum alloy type 5183 which was analyzed in triplicate by the above procedure and by chemical methods (Table III).

TABLE III. TRIPPLICATE ANALYSES OF ALLOY 5183 <sup>a</sup>

Method	Spectrographic			Chemical
Mg	4.9	5.5	5.9	5.1
Mn	0.62	0.60	0.63	0.63
Si	0.55	0.59	0.63	0.5
Cr	0.27	0.21	0.18	0.25
Cu	<0.1	<0.1	<0.1	0.04

<sup>a</sup> All values given in %

### Literature Cited

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\*No. 2000 wrought aluminum alloy swatches obtainable from Spex Industries, Inc., Scotch Plains, N. J.



## Spectroscopic Tricks

### KBr Pellet Holder

Robert A. Pittman

Southern Regional Research Laboratory, U. S. Department of Agriculture, New Orleans, La.

Recently, this Laboratory had reason to scan some KBr pellets, produced in a Beckman Die†, using a Model 14 Cary Recording Spectrophotometer. The problem of mounting the pellets in the instrument beam led to the design and fabrication of two brass holders according to the plans shown in Figure 1. When mounted in the instrument with the cell holders at the approximate center of the sample chamber, the pellet holder will pass the full beam of the instrument. Two pellet holders are used with one containing the sample pellet in the sample beam and the other a blank KBr pellet in the reference beam. Figure 2 shows a holder mounted in the sample chamber of the instrument.

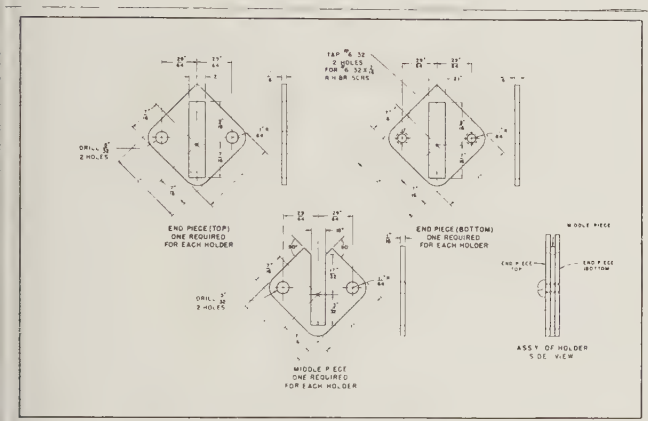


FIG. 1. PLANS FOR KBr PELLET HOLDER

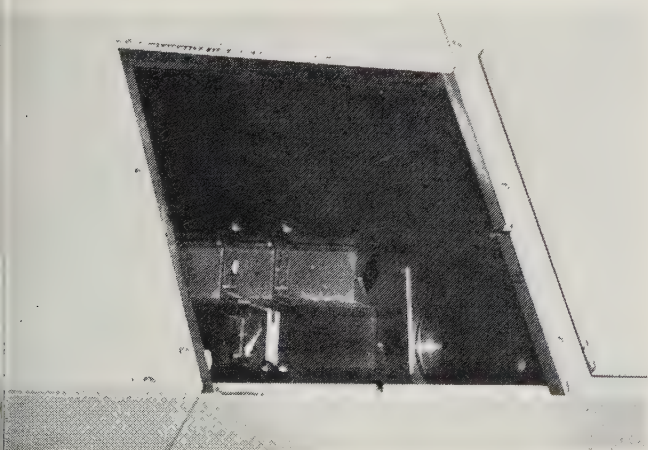


FIG. 2. PELLET HOLDER MOUNTED IN SAMPLE CHAMBER OF INSTRUMENT

†Catalog No. 4240, Beckman Instrument Co., Fullerton, Calif.

Submitted August 4, 1960

## Society News

### Governing Board Meeting February 28, 1961

The Governing Board met in the Penn-Sheraton Hotel in Pittsburgh on Tuesday, February 28, 1961.

Mrs. Sarah H. Degenkolb, the Retiring President, installed Mr. Neil Gordon as President and Mr. John Hansen as President-Elect. She thanked all of the Officers of the Society, the Editors of the journal, the members of the Governing Board, and all members of Committees for the cooperation they had given her in her term of office. The new Officers accepted with thanks the responsibility of their respective offices. Copies of the Annual Report were distributed to the members of the Governing Board. This report included the Treasurer's Report and that of each Committee.

The Executive Committee recommended to the Governing Board the Society for Applied Spectroscopy sponsor only one Spectroscopy Conference each year. The Local Section, which is authorized by the Governing Board, will act as host to the conference in that year. This resolution was not intended to restrict any meetings of Local Sections or Regional Meetings that are sponsored by Local Sections in their own names. It was the intent of the Governing Board that Local Sections should be encouraged to conduct these meetings for the benefit of their members and any persons interested in spectroscopy. However it was felt that this new resolution would cut down on the number of meetings at which Instrument Makers and Suppliers would be expected to show.

The Governing Board approved a resolution to grant Mr. Ted Zink \$250 to inaugurate the proposed International Library. This project will start off as a bibliography of recent papers in all fields of spectroscopy. The source of the titles of these papers will be spectroscopists all over the world who will send the titles to Mr. Zink. For the present these titles will be distributed to subscribers and will be printed in Interlingua. Eventually it will be possible to get translations of these papers in Interlingua at a very reasonable cost. One of the chief values of this project to subscribers will be the publication of the titles within a few months of the publication of the original papers.

Dr. Marvin Margoshes presented a report on the progress of the International Conference on Spectroscopy, 1962. Announcements of further progress will be made through the news columns of Applied Spectroscopy.

The Executive Committee recommended to the Governing Board a division of responsibilities of the Editor-in-Chief and Managing Editor, which seemed most reasonable for the smooth operation of publishing the journal. This division of responsibility became necessary by reason of the fact that Dr. Frederick Strong III moved to the Inter-American University in Puerto Rico.

The following resolution was adopted by the Governing Board: Be it resolved that in matters of major scope any Local Section through its delegate or delegates submit in writing to the Executive Committee, at least one month prior to the next Governing Board Meeting, the proposed new business in order that the Executive Committee may be prepared to make recommendations to the Governing Board or the appropriate Committee on the matter.

The next Meeting of the Governing Board will be held in Chicago at the 12th Annual Symposium on Spectroscopy from May 15-18, 1961. Notice of the time and place will be sent to the Delegates.

## Nominations

Those members wishing to suggest candidates for the offices of President-Elect, Secretary, and Treasurer, should send their suggestions to the Chairman of the Nominating Committee before May 1, 1961. The Committee consists of Mr. Dimetro Andrychuck, Mr. Philip Evans, Mr. Rufus H. Gaddy, Dr. Aldenlee Spell, and Mr. R. K. Scott as Chairman. He is located at Harbison-Walker Refractories Co., Box 98037, Pittsburgh 27, Pa.

## Teachers of Spectroscopy

Those teachers, who are interested in joining a group to exchange ideas, should contact Dr. Leopold May, Dept. of Chemistry, The Catholic University of America, Washington 17, D.C. There will be a session at the International Conference on Spectroscopy, 1962, on this subject.

## International Conference on Spectroscopy

College Park, Md. June 18-22, 1962

Considerable progress has been made in planning the International Conference on Spectroscopy organized by SAS. This will be the first general meeting sponsored by the Society.

The general plan of the conference is for a series of one-hour invited papers at the morning sessions. The invited papers are to be broad in scope and to be presented in non-simultaneous sessions. Afternoon sessions are to consist of invited papers and submitted papers in the following fields of interest: atomic emission and absorption, infrared and Raman, x-ray emission and absorption, mass, NMR, EPR, microwave, and teaching in spectroscopy.

Of great value to the Society in planning this conference are the large number of outstanding spectroscopists who are serving on the conference committee. The following is a partial list of the Conference Officers;

*General Chairman:* Mr. Bourdon F. Scribner, National Bureau of Standards

*International Advisory Board:* Dr. W. F. Meggers, National Bureau of Standards, ret.; Dr. A. C. Menzies, Hilger and Watts, Ltd.

*Program Chairman:* Dr. Ellis R. Lippincott, University of Maryland

*Program Committee:*

Atomic Emission and Absorption

Prof. V. A. Fassel, Iowa State University

Infrared and Raman Spectroscopy

Prof. R. C. Lord, Mass. Institute of Technology

X-Ray Emission and Absorption

Dr. H. A. Liebhafsky, General Electric Co.

NMR, EPR, Microwave Spectroscopy

Prof. C. Hutchinson, University of Chicago

Teaching in Spectroscopy

Prof. E. J. Rosenbaum, Drexel Institute of Technology

*Foreign Visitors Liaison:* Dr. Wallace R. Brode

Those desiring to present papers should submit titles and abstracts of 300 words or less to the Conference Chairman before December 1, 1961. All individuals interested in further details should send their names and addresses to Mr. Bourdon F. Scribner, Conference Chairman, International Spectroscopy Conference, National Bureau of Standards, Washington 25, D. C., U.S.A.

## Central Library of Spectroscopy

The Society, by action of its Governing Board on February 28, 1961, has initiated yet another service to spectroscopists. A long-felt need for the rapid collection and distribution of the literature of spectroscopy will henceforth be filled by the organization of the Central Library of Spectroscopy (Bibliotheca Central de Spectroscopia).

The Library has begun with the collection of papers and the publication of 'titulos spectroscopic', an Interlingua collection of the titles of papers, the names and addresses of their authors, Journal references, and language of publication. This is considered to be the minimum of information needed initially. On the basis of this information, reprints can be requested more readily from authors. If the language of publication proves to be inaccessible to an individual, he may request from the Library an Interlingua translation of the summary, and thus determine whether he would like the entire paper translated. Once translated, any paper (or summary) is immediately accessible to the vast majority of spectroscopists anywhere in the world. No additional translation should be required for any paper.

The time-lag involved in publishing the titles will rarely exceed one month. This speed is made possible primarily by the cooperation of many outstanding spectroscopists in many countries, who have agreed to scan the literature of their own country for the benefit of all spectroscopists.

The information collected, will be cross-indexed in order to facilitate the preparation of bibliographies for special purposes and, on request, within specific fields. The Library is making an effort to obtain copies of all published papers in all fields of spectroscopy, as the time goes on, but will at this time concentrate on recently published material. All spectroscopists throughout the world are invited to make use of the new facilities.

The domestic subscriptions to each part of 'titulos spectroscopic', the 'organic' and the 'inorganic' section, each published once a month, have been set at \$7.00 per year for individual subscribers and \$35.00 per year for libraries. Foreign subscriptions are, of course, accepted with the additional payment of postage, regular or airmail, as requested. Checks should be made payable to "Bibliotheca Central de Spectroscopia", and subscriptions should be sent to 212 Chestnut Hill Drive, Ellicott City, Md., U.S.A.



## Message From The Past President

The black onyx pen set inscribed "Mrs. Sarah H. Degenkolb President 1960 SAS" that was presented to me at the Annual Business Meeting of the Society, March 2, 1961, is deeply appreciated and something that I will always cherish. I want to thank the membership for the gift, the honor and opportunity of serving as their president, and for the excellent cooperation and support that was given to me during my term of office.

Sarah H. Degenkolb











